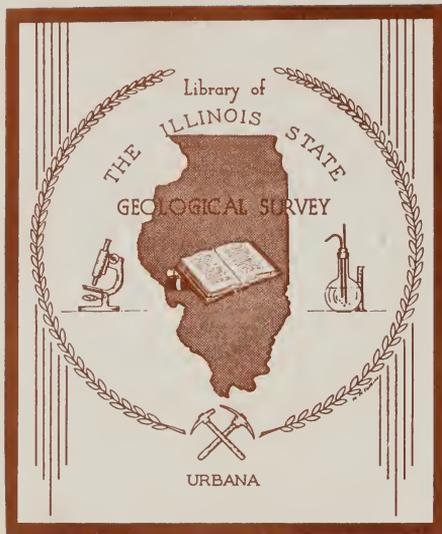


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**ILLINOIS**  
**STATE GEOLOGICAL SURVEY**  
**BULLETIN No. 69**



**ALUMINA EXTRACTION**



ILLINOIS STATE GEOLOGICAL SURVEY



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BULLETIN NO. 69

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AMENABILITY OF VARIOUS TYPES OF  
CLAY MINERALS TO  
ALUMINA EXTRACTION  
BY THE LIME SINTER AND LIME-SODA  
SINTER PROCESSES

By

R. E. GRIM, J. S. MACHIN, AND W. F. BRADLEY

ILLINOIS GEOLOGICAL  
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SINTER PROCESSES

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R. E. GRIM, *Petrographer*  
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INTRODUCTION

THE usual ore from which aluminum is recovered is bauxite, an essentially silica-free alumina hydrate. In order to meet the normal peacetime needs of the United States, it has been necessary to import bauxite. With the outbreak of the war, government agencies at once recognized the seriousness of the situation that would result if bauxite imports were halted and began studies of the possible use of other materials as sources of alumina. Particular attention was directed to clays because they are abundant, they contain considerable quantities of alumina, and a considerable amount of information concerning clays was already in hand.

There are two general processes for extracting alumina from clays: An acid process that uses an acid to selectively dissolve the alumina, usually after the clay has been roasted, and an alkaline process that uses water or a dilute alkaline solution to selectively dissolve the alumina from a sintered mixture of lime and clay or of lime, soda, and clay. Most past experimental work with these processes had been limited to high-alumina clays of the kaolin or bauxitic-kaolin type. A study of the occurrence of clays indicated that deposits of kaolinite clays of sufficient purity and size for an alumina plant are not now known. Kaolinite clays are abundant, but in the main they contain varying, although frequently small,

amounts of other clay minerals. Further, other types of clay, notably the illite shales, are widespread in enormous relatively uniform deposits, and some of them have alumina contents not very much smaller than the average in the large deposits of kaolin.

It became obvious, therefore, that researches were needed on the clay minerals other than kaolinite as possible sources of alumina. Accordingly in January 1943, the War Metallurgy Committee of the National Academy of Sciences suggested that the Illinois State Geological Survey conduct an investigation of the "amenability of clay mineral types to lime sinter and lime-soda sinter alumina processes" for the War Production Board.

The Illinois State Geological Survey had been and still is conducting extensive researches on the clay mineral composition and properties of the clays and shales of Illinois. Since the properties of clay materials in general are controlled largely by their clay mineral composition, the Survey has studied extensively the relation between the clay mineral composition of all types of clays and shales and their properties and uses. The investigation undertaken for the National Academy of Sciences was, therefore, essentially an extension of these researches.

## CLAY MINERAL CONCEPT

Recent researches in several laboratories have shown that natural clay substances are composed of extremely small crystalline particles of members of any one or more of a few groups of minerals known as the "clay minerals." The "clay minerals" (table 1) are hydrous aluminum silicates, frequently with some replacement of aluminum by iron and magnesium and with small amounts of alkalis and alkali earths. In rare instances magnesium and iron completely replace the aluminum. In addition to the "clay minerals," variable but usually small amounts of quartz, limonitic material, gibbsite, diaspore, organic material, pyrite, feldspar, etc., may also be present in clay materials. Grim<sup>1\*</sup> has recently published a summary of the composition, properties, structure and occurrence of the various clay minerals.

TABLE 1.—COMMON CLAY MINERALS

| Name   | Composition formula  |
|--|--|
| Kaolinite group <sup>a</sup> . . .           | (OH) <sub>8</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub>  |
| Illite group <sup>b</sup> . . . . .          | (OH) <sub>4</sub> K <sub>y</sub> (Al <sub>4</sub> ·Fe <sub>4</sub> ·Mg <sub>4</sub> ·Mg <sub>6</sub> )<br>(Si <sub>8-y</sub> ·Al <sub>y</sub> )O <sub>20</sub> |
| Montmorillonite group <sup>c</sup> . . . . . | (OH) <sub>4</sub> Al <sub>4</sub> Si <sub>8</sub> O <sub>20</sub> ·nH <sub>2</sub> O   |
| Hydrated halloysite <sup>d</sup> . . . . .   | (OH) <sub>8</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub> ·2H <sub>2</sub> O   |
| Halloysite . . . . .                         | (OH) <sub>8</sub> Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub>  |
| Attapulgite <sup>e</sup> . . . . .           | (OH <sub>2</sub> ) <sub>4</sub> (OH) <sub>2</sub> Mg <sub>8</sub> Si <sub>8</sub> O <sub>20</sub> ·4H <sub>2</sub> O   |

<sup>a</sup> Dickite and nacrite with the same composition also belong to this group but their occurrence is extremely rare. Anaxite with a slightly higher silica content is usually classified in the kaolinite group—its occurrence is also rare.

<sup>b</sup> As indicated by the formula the composition of the illite group is variable. The y in the formula is frequently equal to about 1. The illite group has not yet been divided into distinct mineral species.

<sup>c</sup> The Al<sup>+++</sup> of the montmorillonite is replaceable by Fe<sup>+++</sup> or Mg<sup>++</sup>. When the replacement is relatively complete the resulting mineral species are nontronite and saponite, respectively.

<sup>d</sup> Hydrated halloysite inverts to halloysite irreversibly at about 60°C.

<sup>e</sup> In attapulgite Al<sup>+++</sup> can replace Mg<sup>++</sup> and Si<sup>+++</sup> to a limited extent.

The type of clay known as kaolin is composed of minute (1 micron ±) crystalline particles of the mineral kaolinite. Some such clays contain also small amounts of montmorillonite and illite. The ceramic ball clays and fireclays are usually composed of kaolinite with small amounts of illite. The high-alumina clays are mixtures of kaolin-

ite and diaspore or gibbsite. Large deposits of halloysite clays are not known, but the mineral may be present in small amounts in many clays that are made up primarily of other clay minerals.

Illite is the dominant mineral in all the shales that have been studied mineralogically. Bentonites are composed primarily of extremely minute particles of montmorillonite, and attapulgite is the component of certain fuller's earths. The clay mineral composition of surficial soil materials is variable depending on the conditions under which the soil has formed and on the parent material.

## OBJECTIVES OF THE INVESTIGATION

Objectives of the investigation were as follows:

1. To determine if any clays other than those composed of kaolinite are promising raw materials for alumina extraction by the alkali methods, and if so how the conditions governing sintering and extraction of other clays differ from those governing the sintering and extraction of kaolinite types.

2. To provide some of the necessary data for the solution of problems that will arise in the large scale use of clays as a source of alumina because of the inevitable variations in clays. It is unlikely that a deposit of any clay, kaolin or some other type, large enough for several years supply of alumina, is to be found anywhere that is composed throughout of a single clay mineral. Variations in kaolin deposits, for example, may be expected by the sporadic occurrence of small amounts of illite or montmorillonite.

3. To throw light on the mechanism of the extraction of alumina from clays by the alkali methods. It seemed probable that the study of a variety of materials might provide clues that would not appear in investigations limited to one type of clay.

After the investigation was started it was enlarged to include the study of the effect on alumina extraction of certain non-clay-mineral impurities apt to be found in clays and of variations in the character of limestone.

\*See references at end of report.

## ACKNOWLEDGMENTS

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the project and their continued interest in the work. They also wish to make acknowledgment to the Project Committee which supervised the project, particularly to its chairman, Mr. John D. Sullivan, for many helpful suggestions and comments.

## MATERIALS STUDIED

## CLAYS

## SELECTION OF SAMPLES

On the basis of a large amount of analytical data in the files of the Illinois State Geological Survey, 19 samples of clay (table 2) were selected to represent the important types of clay minerals and mixtures of these minerals. Particular attention was given to clays containing some kaolinite because such clays tend to have the highest content of alumina. The samples selected to represent mixtures illustrate the

combinations of clay minerals that are apt to be encountered in large deposits of the common types of clays. Further consideration was given to the selection of samples that would represent important types of clay that occur widely in large deposits.

## COLLECTION AND PREPARATION OF SAMPLES

All of the samples except 865, 868, 881, 882, and 883 were collected personally by Drs. Grim and Bradley. About 100 lbs. of each sample was obtained in lump form.

TABLE 2.—LOCATION AND CLAY MINERAL COMPOSITION OF CLAY SAMPLES

| Sample No. | Type of clay     | Location               | Mineral composition   |
|------------|------------------|------------------------|---|
| 865        | Kaolin           | Ringgold, Tenn.        | Kaolinite   |
| 866        | Underclay        | Grundy County, Ill.    | Illite, kaolinite (20%±), quartz (15%±), trace of pyrite, gypsum, and calcite   |
| 867        | Halloysite clay  | Eureka, Utah           | Halloysite and hydrated halloysite, gibbsite (10%±)                             |
| 868        | Bentonite        | Clay Spur, Wyo.        | Montmorillonite, quartz (10%±)  |
| 869        | Kaolin           | Union County, Ill.     | Kaolinite with unusual lattice structure properties, quartz (10%±)              |
| 870        | Shale            | Menard County, Ill.    | Illite (high iron variety), quartz (15%±), trace of pyrite, limonite, kaolinite |
| 871        | Plastic fireclay | Mexico, Missouri       | Kaolinite with small amount of illite, montmorillonite and organic material     |
| 872        | Diaspore         | Swiss, Missouri        | Diaspore, trace of kaolinite, anatase, rutile                                   |
| 873        | Flint clay       | New Florence, Missouri | Kaolinite, trace of anatase and montmorillonite (?)                             |
| 874        | Bauxitic kaolin  | Dry Branch, Ga.        | Kaolinite with small amount of gibbsite, trace of anatase                       |
| 875        | Bauxite          | Irvington, Ga.         | Gibbsite with small amount of kaolinite, trace of anatase                       |
| 876        | Hard kaolin      | Gordon, Ga.            | Kaolinite, very fine grain size, trace of montmorillonite                       |
| 877        | Soft kaolin      | Dry Branch, Ga.        | Kaolinite, medium grain size  |
| 878        | Plastic kaolin   | Dry Branch, Ga.        | Kaolinite, montmorillonite (25%±)   |
| 879        | Ball clay        | Whitlock, Tenn.        | Kaolinite, illite, quartz (10%±), organic material                              |
| 880        | Ball clay        | Atwood, Tenn.          | Kaolinite, illite (?), gibbsite (?)   |
| 881        | Kaolin           | Aiken, S. Carolina     | Kaolinite, trace of alunite   |
| 882        | Fuller's earth   | Quincy, Florida        | Attapulgitite, montmorillonite (10%±)   |
| 883        | Kaolin           | Hobart Butte, Oregon   | Kaolinite with low degree of crystallinity                                      |

TABLE 3.—CHEMICAL COMPOSITION OF CLAY SAMPLES  
(In percent)

| Clay No. | SiO <sub>2</sub> | TiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | Ign. Loss                      | Total  |
|----------|------------------|------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|--------------------------------|--------|
| 865      | 44.41            | 3.30             | 0.58                           | 38.31                          | 0.06 | 0.12 |                   |                  | 13.48                          | 100.26 |
| 866      | 59.40            | 1.48             | 4.50                           | 20.74                          | 1.09 | .92  | 0.34              | 3.84             | 7.60                           | 99.91  |
| 867      | 43.12            | ...              | .50                            | 40.50                          | .05  | .28  | .12               | .11              | 15.71                          | 100.39 |
| 868      | 64.41            | 0.19             | 3.65                           | 20.80                          | 2.33 | .83  | 2.86              | .39              | 4.86                           | 100.32 |
| 869      | 53.20            | 1.44             | 1.44                           | 31.22                          | .52  | .34  | .46               | .34              | 11.53                          | 100.49 |
| 870      | 58.48            | 1.20             | 7.74                           | 20.27                          | 2.00 | .52  | 1.28              | 3.33             | 6.29                           | 101.11 |
| 871      | 56.09            | 1.95             | 2.29                           | 28.34                          | 0.50 | .35  | .28               | 1.79             | 9.03                           | 100.62 |
| 872      | 10.97            | 4.29             | 1.70                           | 68.45                          | .07  | .33  | .69               | 1.10             | 13.10                          | 100.72 |
| 873      | 45.07            | 2.47             | .51                            | 38.58                          | .08  | .17  | .21               | .08              | 13.58                          | 100.75 |
| 874      | 36.15            | 2.10             | .37                            | 44.23                          | .05  | .00  | .18               | .04              | 17.86                          | 100.98 |
| 875      | 24.15            | 2.45             | 1.14                           | 48.87                          | .04  | .00  | .37               | .03              | 22.98                          | 100.03 |
| 876      | 49.75            | 1.87             | 1.21                           | 33.93                          | .29  | .21  | .31               | .58              | 12.02                          | 100.17 |
| 877      | 45.18            | 2.15             | .31                            | 38.80                          | .03  | .00  | .24               | .01              | 13.87                          | 100.59 |
| 878      | 48.81            | 1.72             | .33                            | 35.79                          | .74  | .77  | .13               | .01              | 12.35                          | 100.65 |
| 879      | 48.87            | 1.59             | .94                            | 32.29                          | .63  | .04  | .57               | 1.80             | 13.63                          | 100.36 |
| 880      | 48.34            | 2.08             | .72                            | 35.59                          | .32  | .02  | .51               | .32              | 12.52                          | 100.42 |
| 881      | 46.10            | 1.90             | 1.46                           | 36.49                          | .14  | .03  | .52               | .23              | 13.44                          | 100.31 |
| 882      | 60.98            | .54              | 3.66                           | 11.82                          | 9.60 | 2.25 | .47               | .72              | 10.06                          | 100.10 |
| 883      | 48.64            | 3.07             | 0.45                           | 34.71                          | 0.13 | .12  | .31               | .01              | 12.54                          | 100.18 |
|          |                  |                  |                                |                                |      |      |                   |                  | As <sub>2</sub> O <sub>3</sub> | .20    |

TABLE 4.—LOCATION AND TEXTURE OF LIMESTONE SAMPLES

| Sample No. | Age and Location                          | Size of calcite particles  |
|------------|---|--|
| R7         | St. Louis limestone, Alton, Illinois      | Maximum diameter 5 microns; most particles less than 3 microns     |
| R2         | St. Louis limestone, Alton, Illinois      | Maximum diameter 15 microns; particles range from 3 to 15 microns  |
| MC         | Burlington limestone Marblehead, Illinois | Maximum diameter 70 microns; most particles larger than 20 microns |

A small quantity of the lump material of each sample was retained for reference, and and the remainder was ground to minus 10-mesh in a disk pulverizer in order to obtain thorough mixing. Ten-pound lots of each sample were ground further to minus 80-mesh in preparation for chemical analysis and sinter experiments.

ANALYSIS OF SAMPLES

The clay mineral composition of each sample was determined by X-ray diffraction, differential thermal, and optical analyses with the results given in table 2. Chemical analyses of all samples are given in table 3.

LIMESTONE

Precipitated CaCO<sub>3</sub> was used in preparing all of the sinters except those especially made to investigate the effect of variations in the textural character of the limestone on alumina extraction. For this purpose three limestones were selected. Table 4 gives the location of the limestones and the size of the particles of calcite that make up each of them. Chemical analyses of the limestones are given in table 5.

ANORTHOSITE

Anorthosite was included in the part of the investigation concerned with lime-soda sinters. A sample was supplied by Mr. D.

R. Williams of the Monolith Portland Midwest Company from a deposit near Laramie, Wyoming. A chemical analysis of the sample is given in table 6. Mineralogically the anorthosite is composed of a plagioclase feldspar of about labradorite composition.

TABLE 5.—CHEMICAL COMPOSITION OF LIMESTONE SAMPLES (In percent)

|                                | R7     | R2     | MC     |
|--------------------------------|--------|--------|--------|
| SiO <sub>2</sub>               | 2.59   | 0.46   | 0.35   |
| TiO <sub>2</sub>               | .02    | .02    | .00    |
| Al <sub>2</sub> O <sub>3</sub> | .55    | .27    | .14    |
| Fe <sub>2</sub> O <sub>3</sub> | .14    | .14    | .07    |
| MgO                            | .33    | .23    | .27    |
| CaO                            | 53.77  | 55.36  | 55.65  |
| Na <sub>2</sub> O              | .06    | .05    | .08    |
| K <sub>2</sub> O               | .07    | .03    | .00    |
| P <sub>2</sub> O <sub>5</sub>  | .00    | .00    | .00    |
| SO <sub>3</sub>                | .14    | .06    | .04    |
| Loss on Ign.                   | 42.53  | 43.67  | 43.72  |
| Total                          | 100.20 | 100.29 | 100.32 |
| H <sub>2</sub> O-(<110°C.)     | .24    | .08    | .11    |
| CO <sub>2</sub>                | 42.30  | 43.51  | 43.69  |

TABLE 6.—CHEMICAL COMPOSITION OF ANORTHOSITE SAMPLE (In percent)

|                                |       |                   |       |                               |        |
|--------------------------------|-------|-------------------|-------|-------------------------------|--------|
| SiO <sub>2</sub>               | 52.50 | MgO               | 0.21  | P <sub>2</sub> O <sub>5</sub> | 0.08   |
| TiO <sub>2</sub>               | .23   | CaO               | 11.71 | Loss on Ign.                  | .32    |
| Fe <sub>2</sub> O <sub>3</sub> | 2.28  | Na <sub>2</sub> O | 3.94  | Total                         | 100.16 |
| Al <sub>2</sub> O <sub>3</sub> | 28.48 | K <sub>2</sub> O  | .43   |                               |        |

## LIME-SINTER PROCESS

This process in brief consists in mixing ground siliceous alumina bearing ore with ground calcium carbonate in the proportions to give a mixture corresponding approximately in percentage composition (ignoring volatile constituents present) to a mixture of dicalcium silicate and pentacalcium trialuminate. This mixture is then heated at a suitable temperature (of the order  $1375^{\circ}\text{C}.$ ) and for such period of time as may be necessary to develop dicalcium silicate and some calcium aluminate compound or compounds which can be acted upon by dilute alkali carbonate solution in such manner as to dissolve alumina and leave undissolved all or nearly all of the silica, lime, and any other materials present in the sintered material. The dicalcium silicate plays an extremely important dual role. First, its development is complete enough to tie up nearly all of the silica present in a form not soluble in the leach liquor. Second, it undergoes a crystallographic transformation on cooling below about  $675^{\circ}\text{C}.$  with an increase in volume which results in reduction of the sintered mass to a powder, making the soluble alumina compounds easily accessible to the action of the leach liquor without grinding. This phenomenon is commonly called "dusting."

The clay samples used in these experiments after mixing with  $\text{CaCO}_3$  and heating gave sintered materials in which the composition ranged about as follows in most cases:

|                         |                  |
|-------------------------|------------------|
| $\text{Al}_2\text{O}_3$ | 10 to 30 percent |
| $\text{CaO}$            | 52 to 62 percent |
| $\text{SiO}_2$          | 14 to 28 percent |

The fusion points of mixtures represented by such ranges in composition are well above  $1375^{\circ}\text{C}.$  so that in general, it is to be expected that a state of chemical equilibrium will be approached but not reached unless the mixtures are kept at the sintering temperature for very long periods of time. The longer the period of time and the higher the temperature, the closer will be the

approach to a state of equilibrium. The presence of varying, even though minor, amounts of alkalis, iron, magnesia, phosphorus, and titania also might be expected, through fluxing action or otherwise, to influence the final state reached. Finally the various clay minerals, with their differences in reactivity and refractoriness might be expected to exert a major effect, at least up to some critical temperature which would probably be different for each clay mineral type. This critical temperature might be the fusion point of the sinter mixture or might be a lower temperature. The data presented in this report were collected from experiments designed to study the influence of these factors on the lime-sinter process.

The equilibrium diagram of the ternary system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  of Rankin and Wright as revised by Schairer<sup>9</sup> (page 76) is included for the convenience of the reader in visualizing the compositions of the sinters discussed in the lime-sinter section of this report. The shaded section includes the range of compositions included in our experiments.

## EXPERIMENTAL METHODS

## PREPARATION OF SINTER SAMPLES

All of the clay samples except 865 and 872 were calcined at  $800^{\circ}\text{C}.$  Sample 872 was not calcined because calcination of diasporic clay results in crystal changes that take place below  $800^{\circ}\text{C}.$  which it was desired to avoid. Sample 865 was the clay used most extensively in certain experiments at the T. V. A. laboratory,<sup>3</sup> and it was desired to follow their experimental method. In this instance the calcination temperature was  $900^{\circ}\text{C}.$

Calcined clays were ground to pass 80-mesh sieves and then mixed thoroughly with the desired quantity of precipitated calcium carbonate and enough water to make a good briquet. The mixtures were pressed into cylindrical briquets about  $1\frac{3}{8}$  inches in diameter under a pressure of

approximately 5000 pounds per square inch. These briquets were dried, placed in a cold Globar-heated furnace, heated up to the desired temperature, and held for a chosen period at that temperature. The cooling rate was such that approximately 30 minutes elapsed while the furnace cooled down to 1100°C. After this the power was turned off. The sintered briquets were removed from the furnace when the temperature had dropped to about 700°–800°C. and were stored in closed bottles as soon as they were cool enough to handle. Usually the briquets dusted in the cooling process.

Most sinters prepared as described dusted to a powder which easily passed a 200-mesh screen with one percent or less oversize. A few had considerable plus 200-mesh material. Some of those which did not so disintegrate were ground to pass 200 mesh and subsequently extracted in the same manner as the others.

#### CHEMICAL ANALYSIS OF SINTERS

The sintered material was analyzed by gravimetric methods for  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . About three quarters of all sinters were so analyzed.

#### EXTRACTION OF ALUMINA FROM SINTERED MATERIAL AND ANALYSIS OF EXTRACTS

The extraction procedure used was basically similar to that used by Walthall<sup>2</sup> and coworkers at the T. V. A. laboratory, Wilson Dam, Alabama. Ten-gram samples of each sinter were extracted with three percent sodium carbonate solution using mechanical stirring sufficiently vigorous to prevent settling. The extraction time was 15 minutes and the temperature was 65°C. Sufficient sodium carbonate solution was used to provide 1.66 moles of  $\text{Na}_2\text{CO}_3$  for each mole of  $\text{Al}_2\text{O}_3$  calculated to be present in the 10-gram sample. The extract was immediately filtered off and the residue washed. The extract was analyzed for alumina and silica using gravimetric methods for alumina and colorimetric methods for silica.

## EXPERIMENTAL RESULTS

### EFFECT OF TYPE OF CLAY MINERALS OPTIMUM YIELD OF ALUMINA

The factors which may be varied at the will of the operator of a plant producing alumina by the lime-sinter process are the lime-to-clay ratio, the temperature, the duration of the heating period, and to a much lesser extent the furnace atmosphere. Proper adjustment of these variables with relation to one another might be expected to result in an optimum yield for a given raw material, assuming good extraction practice. Data are presented in graphic and tabular form in figures 1 and 2, and in tables 7, 8, and 9 which bear on the effect of these operating variables when the various types of clays are used in the sinter mix under laboratory conditions. Variables connected with the extraction process were not considered in these experiments except that care was taken to keep the extraction conditions constant.

The data indicate that gibbsite-kaolinite clays and kaolinite clays may yield above (some well above) 90 percent of their alumina with little to choose between them. Note data on clay samples, 865, 869, 873, 874, 875, 876, 877, 880, and 881.

Clay sample 883 did not quite measure up to the other kaolinite clays in yield of alumina. Two possible causes of the lower yields from this clay can be suggested; the first and more probable is that it differed considerably from the typical kaolins insofar as its content of true kaolinite is concerned; second, the titania content was rather high. Clay sample 865 also had rather high titania content and gave slightly lower yields than some of the best kaolinite clays. It is not clear, however, why titania should cause lower yields. The presence of calcium titanate in the sinters (see page 38) suggests that better yields might be expected with the higher lime-to-clay ratios, but this suggestion is not confirmed experimentally. Impure kaolins, containing illite and/or montmorillonite, gave lower yields roughly in proportion to the amounts of these clay minerals present.

The illite and montmorillonite clays gave lower percentage yields than the

kaolinite clays although it is not proved that this was due to the clay mineral type. Sinters made with such clays tended to dust slowly and poorly, possibly because of their high alkali content. That is, the dusted sinter contained larger amounts of coarse sandy material. The iron, as indicated in another part of the report, appeared in the sinter as tetracalcium alumino ferrite from which alumina is not readily extractable with dilute sodium carbonate solutions. The illites reacted adversely to low lime ratios (fig. 1, samples 866 and 870), probably because of their high iron content.

Halloysite clay gave low yields except at very high temperatures. This clay contained remarkably small amounts of oxides other than alumina and silica. The sinters prepared from it dusted fairly quickly but incompletely and contained much coarse sandy material, indicating either incomplete inversion of dicalcium silicate, incomplete reaction between the clay and the lime, or the presence of stable glass.

Diaspore clay gave very unsatisfactory sinters. Attempts to sinter it with lime at temperatures above 1300°C. resulted in partially fused glassy masses which did not dust. Upon grinding through 200 mesh these sinters yielded about 70 percent of their alumina. Both the fusion and the failure to dust were expected. The sinters prepared from this clay contained 6 to 7 percent silica, about 40 percent alumina, 48 to 50 percent lime, and the balance iron, titania, and alkalis. The fusion point of such a composition should be below 1335°C., and it is not surprising that the relatively small amount of dicalcium silicate that could be formed should be insufficient to cause dusting.

Attempts to prepare sinters from the attapulgite clay resulted in cinder-like masses which disintegrated slowly into coarse sand-like particles. These sinters were so unpromising that no further work was done on this clay.

#### LIME-ALUMINA RATIO

Data presented graphically in figure 1 show the effect of varying the  $\text{CaO}/\text{Al}_2\text{O}_3$

ratio on the percentage of alumina extracted from different types of clay. The  $\text{CaO}/\text{Al}_2\text{O}_3$  ratios consider only that part of the total  $\text{CaO}$  above that required to react with the silica to produce dicalcium silicate. These same data are listed in table 7 together with the analyses of the sintered materials and of the clays from which they were prepared.

The data show that in general pure kaolinite clays are not very sensitive to moderate variation in the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio. Ratios between 1.5 and 1.8 appear to be favorable for most kaolins, whereas ratios outside these limits usually result in lower yields of alumina.

Illite clays, probably because of high iron, sometimes show considerable improvement in yield with increased lime (note sample 870 in figure 1). Illite sample 866, which gave a low yield with a  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio of 1.4, showed an increase in yield when the ratio was increased to 1.5, but no further increase with larger amounts of  $\text{CaO}$ .

Neither the halloysite clay, nor the montmorillonite clay showed any decided sensitivity to the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio. The data were somewhat erratic. Such erratic extraction values are common if the dusting is incomplete, as it was with most sinters prepared from these two clays.

Gibbsite-kaolinite (bauxitic) clays behaved very much like the pure kaolinites. Like these clays, they reacted unfavorably to much excess lime.

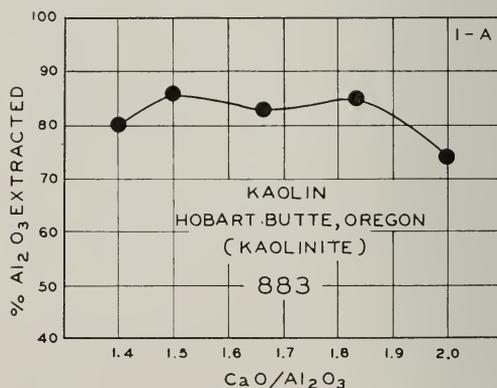


FIG. 1.—Part A  
Percent  $\text{Al}_2\text{O}_3$  extracted versus mole ratio  $\text{CaO}/\text{Al}_2\text{O}_3$  (considering only that part of the  $\text{CaO}$  beyond that required to react with the silica to form  $2\text{CaO} \cdot \text{SiO}_2$ ). Sinter temperature 1360°

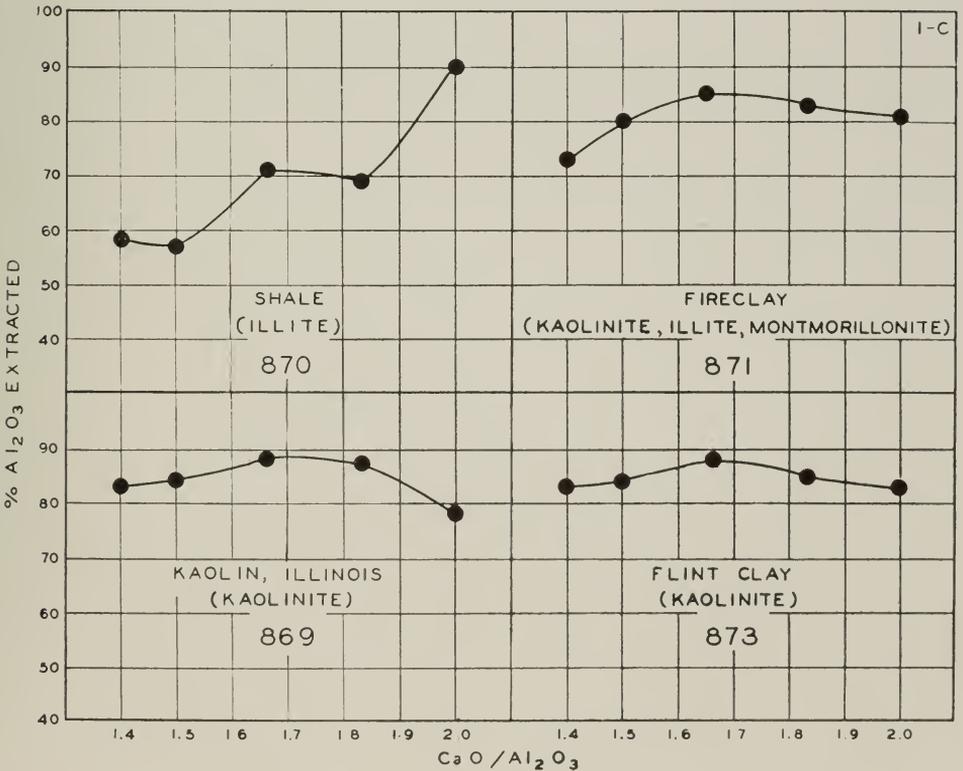
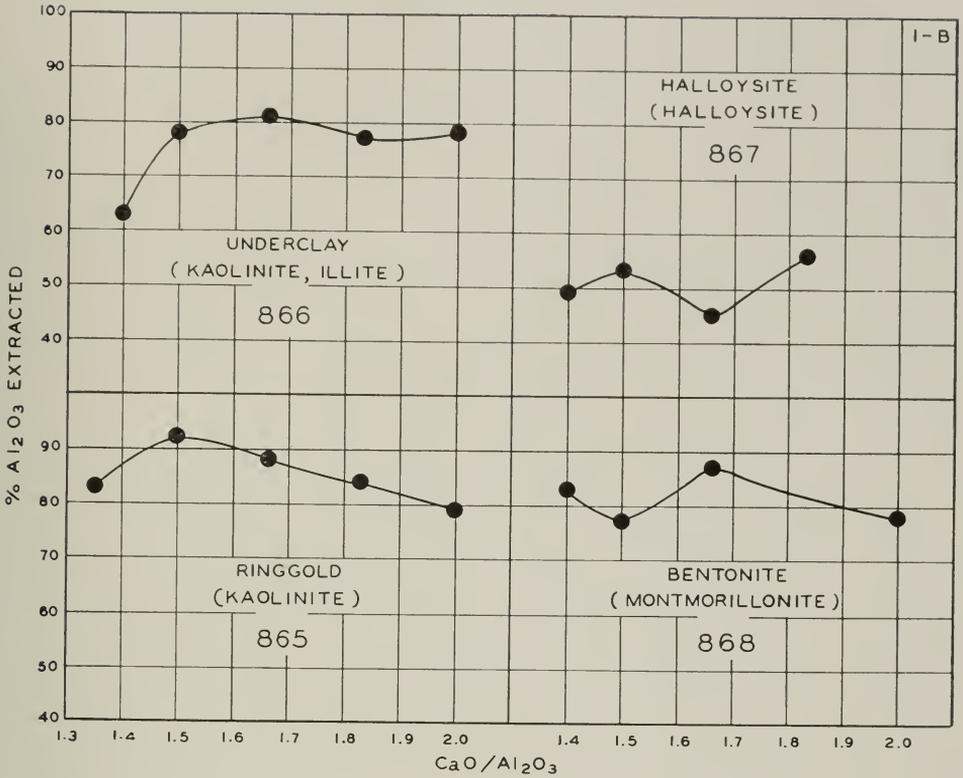


FIG. 1.—Parts B and C  
 Percent  $Al_2O_3$  extracted versus mole ratio  $CaO/Al_2O_3$  (considering only that part of the  $CaO$  beyond that required to react with the silica to form  $2CaO.SiO_2$ ). Sinter temperature  $1360^\circ C$ .

## ALUMINA EXTRACTION

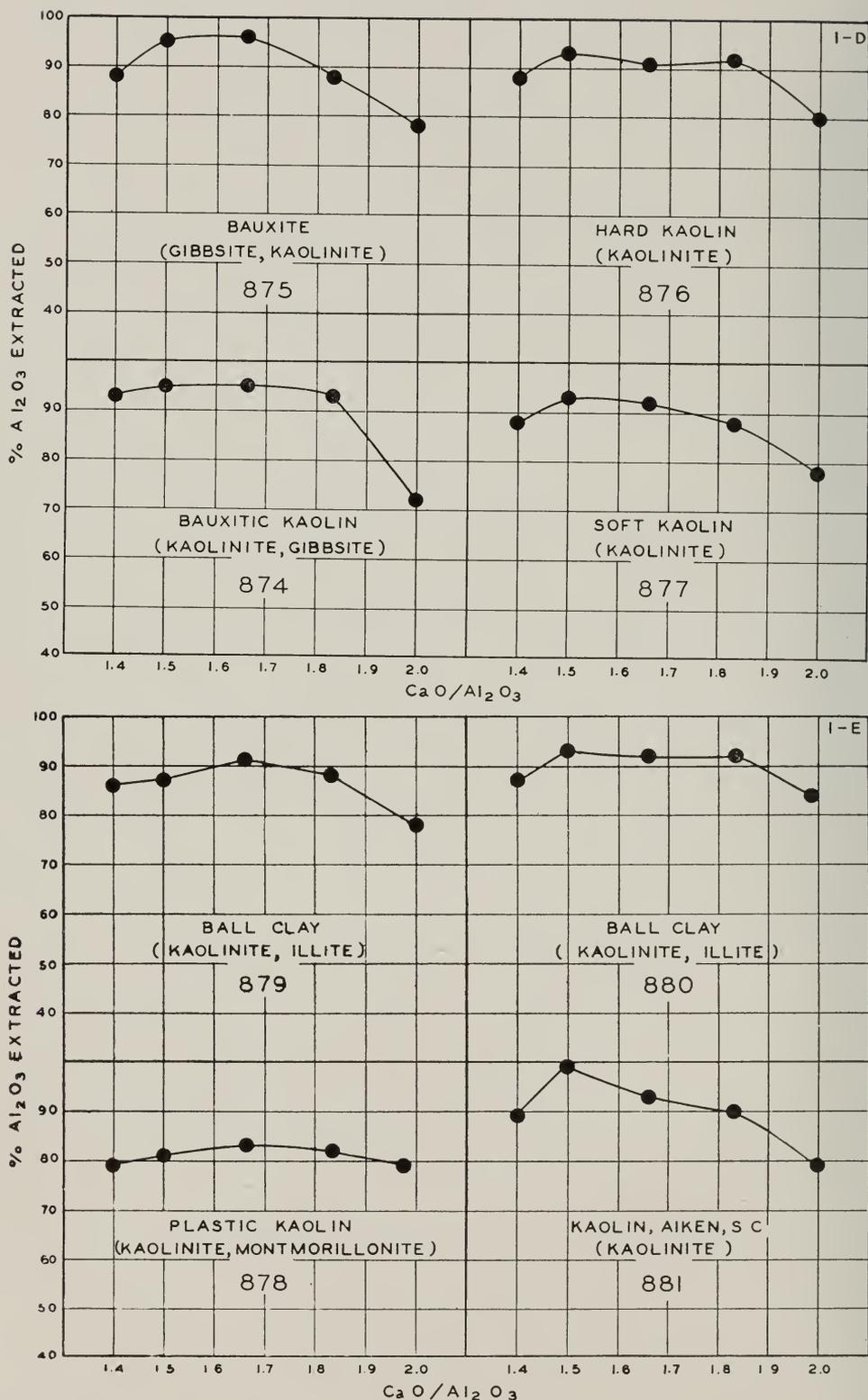


FIG. 1.—Parts D and E

Percent  $\text{Al}_2\text{O}_3$  extracted versus mole ratio  $\text{CaO}/\text{Al}_2\text{O}_3$  (considering only that part of the  $\text{CaO}$  beyond that required to react with the silica to form  $2\text{CaO}\cdot\text{SiO}_2$ ). Sinter temperature  $1360^\circ\text{C}$ .

## SINTERING TEMPERATURE

The data presented in table 7 and figure 2 indicate that for most clays sintering temperatures between 1340° and 1380°C. are favorable. Higher temperatures are with few exceptions not necessary unless for the purpose of shortening sintering time.

Kaolinite clays usually give good yields when sintered at 1360° to 1380°C. There was a pronounced tendency to show a decreased yield with lowered sintering temperature which sometimes was manifest at 1340°C. (869, 873, 876, 877, 883), and sometimes not until somewhat lower temperatures were reached (865, 871, 874, 878, 879, 880, 881). Sinters prepared from pure kaolinite clays showed little or no tendency to overburn.

Sinter mixes prepared from gibbsite-kaolinite and diasporite clays, due to their high alumina and low silica content, were apt to melt. The composition of sinters prepared from sample 875 — if only alumina, lime and silica are considered — should not have melted much below 1600°C. However, the small amounts of other oxides present lowered the fusion point of the mixture considerably. All sinters from sample 875 melted partially when the sintering temperatures were only as high as 1360°C. As stated above, sinters from the diasporite clay melted at even lower temperatures.

Sinters prepared from illite and mont-

morillonite clays were somewhat sensitive to sintering temperature. They appeared to give lowered yields with temperatures on either side of an optimum which was in the range 1360° to 1380°C. They showed a definite tendency to overburn at higher temperatures.

Sinters prepared from halloysite clay had to be heated to high temperatures in order to give even moderately good yields. Even when heated to 1450°C. where fusion or semifusion took place the disintegrated sinter still felt somewhat gritty.

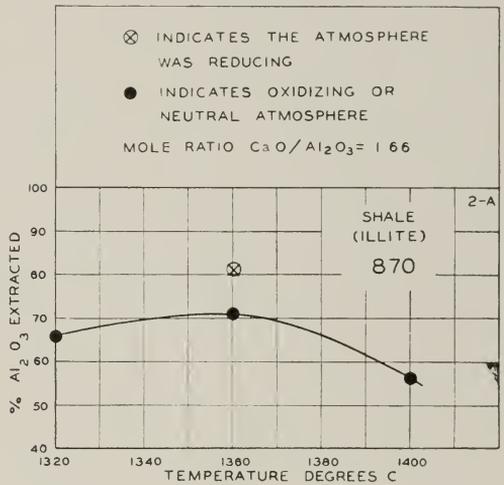


FIG. 2.—Part A  
Percent  $\text{Al}_2\text{O}_3$  extracted from sinter versus temperature at which sinter was held for one hour.

## ALUMINA EXTRACTION

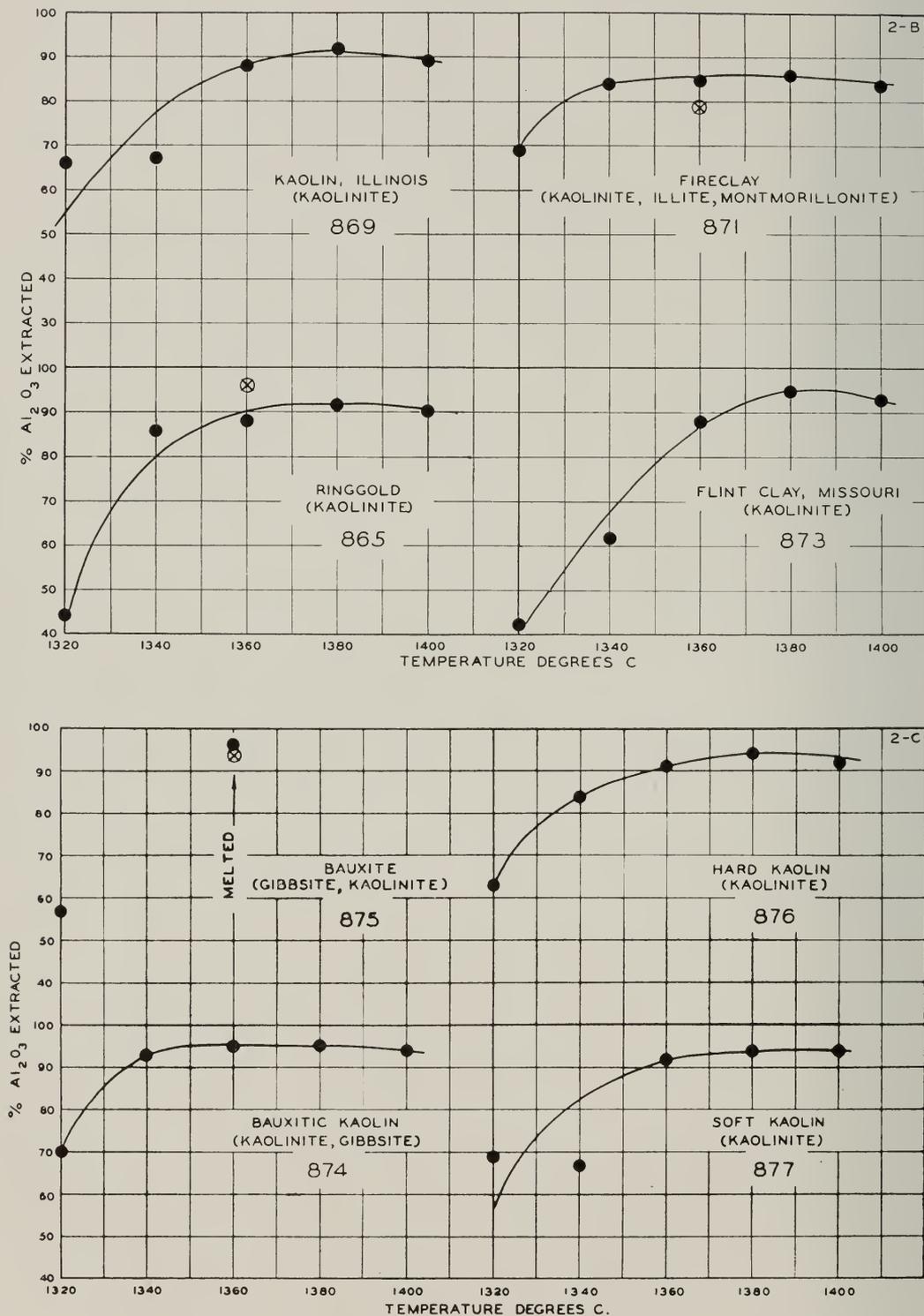


FIG. 2.—Parts B and C  
Percent  $\text{Al}_2\text{O}_3$  extracted from sinter versus temperature at which sinter was held for one hour.

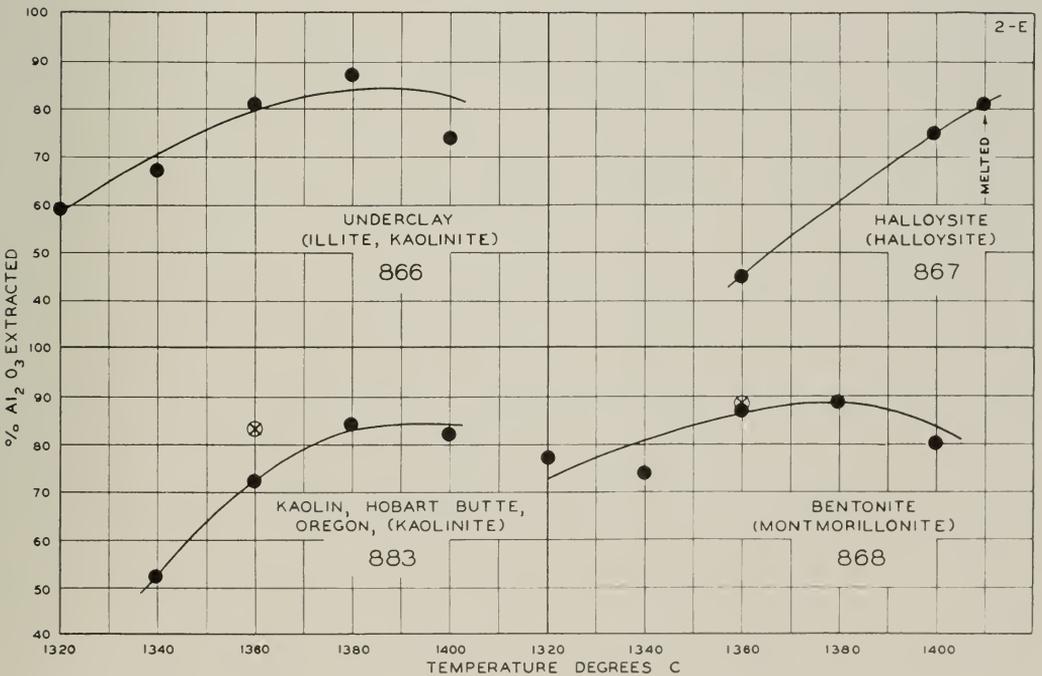
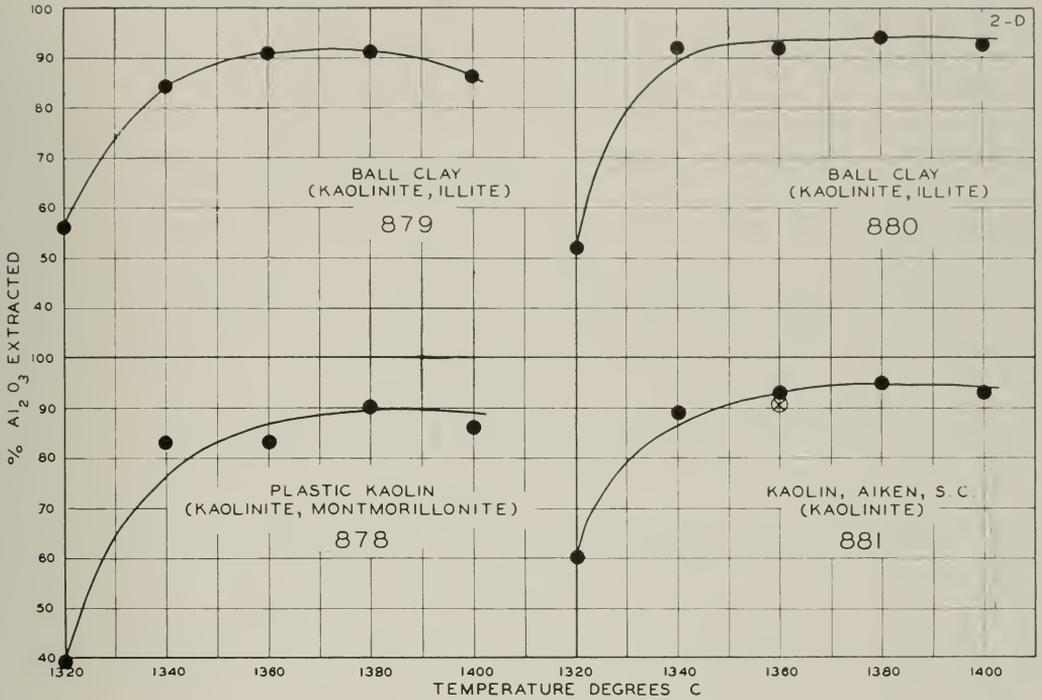


FIG. 2.—Parts D and E  
Percent  $Al_2O_3$  extracted from sinter versus temperature at which sinter was held for one hour.

TABLE 7.—SINTER COMPOSITION AND EXTRACTION DATA

|          | SiO <sub>2</sub><br>% | Al <sub>2</sub> O <sub>3</sub><br>% | CaO<br>% | Fe <sub>2</sub> O <sub>3</sub><br>% | TiO <sub>2</sub><br>% | Total Na <sub>2</sub> O, K <sub>2</sub> O<br>and MgO | %Al <sub>2</sub> O <sub>3</sub><br>ex-<br>tracted | Wt. SiO <sub>2</sub><br>from 10<br>grams | 100 x SiO <sub>2</sub><br>SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub><br>in extract | Mole<br>Ratio<br>CaO:Al <sub>2</sub> O <sub>3</sub> | Sinter<br>Temp.<br>°C. |
|----------|-----------------------|-------------------------------------|----------|-------------------------------------|-----------------------|--|---|--|--|---|------------------------|
| Clay 865 | 51.1                  | 44.0                                | 0.1      | 0.7                                 | 3.8                   | 0.06   |   |  |  |   |                        |
| Sinter   | 24                    | 19.6                                | 56.2     | .3                                  | 1.6                   | .3   | 83  | .030                                     | 1.8  | 1.35  | 1360                   |
| "        | 14                    | 19.6                                | 56.9     | .4                                  | 1.3                   | .3   | 92  | .014                                     | 1.0  | 1.50  | "                      |
| "        | 12                    | 19.2                                | 57.7     | .4                                  | 1.3                   | .3   | 88  | .020                                     | 1.2  | 1.66  | "                      |
| "        | 13                    | 19.2                                | 58.1     | .3                                  | 1.3                   | .3   | 84  | .014                                     | .9   | 1.83  | "                      |
| "        | 125                   | 17.8                                | 59.3     | .3                                  | 1.3                   | .3   | 79  | .021                                     | 1.5  | 2.00  | "                      |
| "        | 156                   | 18.7                                | 57.7     | .3                                  | 1.4                   | .3   | 44  | .024                                     | 2.8  | 1.66  | 1320                   |
| "        | 38                    | 18.9                                | 57.7     | .3                                  | 1.3                   | .3   | 86  | .032                                     | 1.9  | 1.66  | 1340                   |
| "        | 37                    | 21.8                                | 57.6     | .3                                  | 1.5                   | .3   | 92  | .023                                     | 1.3  | 1.66  | 1380                   |
| "        | (178)*                | 18.5                                | 57.7     | .3                                  | 1.6                   | .3   | 91  | .030                                     | 1.7  | 1.66  | 1400                   |
| "        | (193)                 | 18.5                                | 57.7     | .3                                  | 1.6                   | .3   | 96  | .030                                     | 1.7  | 1.66  | 1360                   |
| Clay 866 | 63.8                  | 22.3                                | 1.0      | 4.8                                 | 1.6                   | 5.6  |   |  |  |   |                        |
| Sinter   | 70                    | 9.9                                 | 58.0     | 2.1                                 | .5                    | 2.6  | 63  | .016                                     | 2.5  | 1.40  | 1360                   |
| "        | 15                    | 26.8                                | 57.6     | 2.1                                 | .5                    | 2.6  | 78  | .010                                     | 1.3  | 1.50  | "                      |
| "        | 16                    | 26.5                                | 58.4     | 2.2                                 | .5                    | 2.6  | 81  | .008                                     | 1.0  | 1.66  | "                      |
| "        | 17                    | 26.4                                | 58.6     | 2.5                                 | .5                    | 2.6  | 77  | .006                                     | .8   | 1.83  | "                      |
| "        | 126                   | 26.7                                | 60.3     | 2.0                                 | .5                    | 2.6  | 78  | .013                                     | 1.7  | 2.00  | "                      |
| "        | 157                   | 9.4                                 | 58.8     | 2.0                                 | .5                    | 2.6  | 59  | .016                                     | 2.8  | 1.66  | 1320                   |
| "        | (207)                 | 26.8                                | 58.6     | 2.1                                 | .7                    | 2.6  | 67  | .018                                     | 2.9  | 1.66  | 1340                   |
| "        | 117                   | 27.3                                | 60.3     | 2.1                                 | .5                    | 2.6  | 87  | .020                                     | 2.4  | 1.66  | 1380                   |
| "        | (179)                 | 27.3                                | 60.3     | 2.1                                 | .5                    | 2.6  | 74  | .016                                     | 2.3  | 1.66  | 1400                   |
| Clay 867 | 50.4                  | 47.4                                | .3       | .6                                  | 0                     | .3   |   |  |  |   |                        |
| Sinter   | 71                    | 20.6                                | 57.1     | .3                                  | 0                     | .4   | 49  | .028                                     | 2.7  | 1.40  | 1360                   |
| "        | 21                    | 21.9                                | 57.2     | .3                                  | 0                     | .4   | 53  | .020                                     | 1.8  | 1.50  | "                      |
| "        | 22                    | 20.0                                | 59.3     | .3                                  | 0                     | .4   | 45  | .020                                     | 2.2  | 1.66  | "                      |
| "        | 23                    | 20.4                                | 58.4     | .3                                  | 0                     | .4   | 57  | .020                                     | 1.7  | 1.83  | "                      |
| "        | 93                    | 19.3                                | 60.1     | .3                                  | 0                     | .4   | 75  | .034                                     | 2.5  | 1.66  | 1400                   |
| "        | (204)                 | 19.9                                | 58.1     | .3                                  | 0                     | .4   | 81  | .036                                     | 2.2  | 1.66  | 1450                   |
| Clay 868 | 67.2                  | 21.7                                | .9       | 3.8                                 | .2                    | 5.8  |   |  |  |   |                        |
| Sinter   | 72                    | 9.4                                 | 58.6     | 1.6                                 | .1                    | 3.2  | 83  | .016                                     | 2.0  | 1.40  | 1360                   |
| "        | 18                    | 27.7                                | 59.0     | 1.6                                 | .1                    | 3.2  | 77  | .014                                     | 1.8  | 1.50  | "                      |
| "        | 19                    | 27.6                                | 59.2     | 1.6                                 | .1                    | 3.2  | 87  | .010                                     | 1.2  | 1.66  | "                      |
| "        | 128                   | 27.3                                | 61.2     | 1.6                                 | .1                    | 3.2  | 78  | .009                                     | 1.3  | 2.00  | 1320                   |
| "        | 158                   | 8.8                                 | 60.1     | 1.5                                 | .1                    | 3.2  | 77  | .016                                     | 2.3  | 1.66  | 1340                   |
| "        | (208)                 | 8.8                                 | 60.1     | 1.5                                 | .1                    | 3.2  | 68  | .018                                     | 2.9  | 1.66  |                        |

|          |       |      |      |      |     |     |     |    |      |     |      |      |
|----------|-------|------|------|------|-----|-----|-----|----|------|-----|------|------|
| Sinter   | (195) | 27.1 | 8.8  | 60.1 | 1.5 | .1  | 3.2 | 88 | .014 | 1.8 | 1.66 | 1360 |
| "        | 118   | 27.8 | 9.2  | 60.6 | 1.6 | .1  | 3.2 | 89 | .016 | 1.9 | 1.66 | 1380 |
| "        | (180) | 27.8 | 9.2  | 60.6 | 1.6 | .1  | 3.2 | 80 | .018 | 2.5 | 1.66 | 1400 |
| Clay 869 | Ign.  | 59.2 | 34.7 | 4    | 1.6 | 1.6 | 1.5 |    |      |     |      |      |
| Sinter   | 81    | 25.2 | 15.1 | 58.8 | .8  | .7  | .9  | 83 | .030 | 2.3 | 1.40 | 1360 |
| "        | 55    | 25.0 | 14.5 | 58.6 | .7  | .7  | .9  | 84 | .027 | 2.2 | 1.50 | "    |
| "        | 56    | 24.8 | 14.6 | 58.8 | .6  | .7  | .9  | 88 | .018 | 1.4 | 1.66 | "    |
| "        | 57    | 24.1 | 14.6 | 59.2 | .7  | .7  | .9  | 87 | .006 | .5  | 1.83 | "    |
| "        | 129   | 23.9 | 13.8 | 60.3 | .7  | .6  | .9  | 78 | .016 | 1.5 | 2.00 | "    |
| "        | (159) | 24.6 | 14.3 | 58.9 | .7  | .7  | .9  | 66 | .026 | 2.7 | 1.66 | 1320 |
| "        | (209) | 24.6 | 14.3 | 58.9 | .7  | .7  | .9  | 67 | .026 | 2.7 | 1.66 | 1340 |
| "        | 124   | 24.8 | 14.3 | 59.3 | .7  | .7  | .9  | 92 | .019 | 1.4 | 1.66 | 1380 |
| "        | 181   | 24.8 | 14.3 | 58.7 | .7  | .7  | .9  | 89 | .020 | 1.5 | 1.66 | 1400 |
| Clay 870 | Ign.  | 61.3 | 21.3 | 6    | 8.1 | 1.3 | 6.9 |    |      |     |      |      |
| Sinter   | 73    | 27.4 | 9.4  | 57.2 | 3.4 | .5  | 3.2 | 58 | .020 | 3.5 | 1.40 | 1360 |
| "        | 25    | 26.9 | 9.5  | 56.8 | 3.5 | .5  | 3.2 | 57 | .017 | 3.0 | 1.50 | "    |
| "        | 26    | 26.6 | 9.5  | 57.0 | 3.6 | .5  | 3.2 | 71 | .016 | 2.3 | 1.66 | "    |
| "        | 27    | 26.7 | 9.5  | 58.1 | 3.3 | .5  | 3.2 | 69 | .016 | 2.5 | 1.83 | "    |
| "        | 130   | 26.8 | 8.9  | 59.7 | 3.5 | .5  | 3.2 | 90 | .006 | .7  | 2.00 | "    |
| "        | 196   | 27.3 | 9.3  | 60.0 | 3.5 | .5  | 3.2 | 81 | .016 | 2.1 | 1.66 | "    |
| "        | (160) | 26.3 | 9.1  | 57.4 | 3.5 | .6  | 3.2 | 66 | .018 | 2.9 | 1.66 | 1320 |
| "        | 182   | 26.4 | 8.8  | 57.1 | 3.2 | .5  | 3.2 | 56 | .014 | 2.8 | 1.66 | 1400 |
| Clay 871 | Ign.  | 60.8 | 30.7 | 4    | 2.5 | 2.1 | 2.8 |    |      |     |      |      |
| Sinter   | 74    | 26.1 | 13.6 | 58.1 | 1.1 | .8  | 1.4 | 73 | .023 | 2.3 | 1.40 | 1360 |
| "        | 28    | 25.6 | 13.5 | 57.9 | 1.1 | .7  | 1.4 | 80 | .021 | 1.9 | 1.50 | "    |
| "        | 29    | 25.2 | 13.3 | 58.9 | 1.1 | .7  | 1.4 | 85 | .012 | 1.0 | 1.66 | "    |
| "        | 30    | 24.9 | 13.3 | 59.4 | 1.1 | .7  | 1.4 | 83 | .009 | .8  | 1.83 | "    |
| "        | 131   | 25.0 | 12.8 | 60.8 | 1.0 | .7  | 1.4 | 81 | .008 | .8  | 2.00 | "    |
| "        | 197   | 25.9 | 12.9 | 59.4 | .7  | .7  | 1.4 | 79 | .024 | 2.3 | 1.66 | "    |
| "        | 161   | 25.2 | 13.3 | 58.8 | 1.0 | .7  | 1.4 | 69 | .022 | 2.3 | 1.66 | 1320 |
| "        | (210) | 25.3 | 12.6 | 58.7 | 1.1 | .9  | 1.4 | 84 | .022 | 2.0 | 1.66 | 1340 |
| "        | 119   | 25.6 | 13.2 | 59.9 | 1.0 | .7  | 1.4 | 86 | .023 | 2.0 | 1.66 | 1380 |
| "        | (183) | 25.3 | 12.6 | 58.7 | 1.1 | .9  | 1.4 | 84 | .021 | 1.9 | 1.66 | 1400 |
| Clay 873 | Ign.  | 51.3 | 43.9 | 2    | .6  | 2.8 | .4  |    |      |     |      |      |
| Sinter   | 76    | 22.9 | 19.7 | 56.8 | .2  | 1.3 | .4  | 83 | .036 | 2.2 | 1.40 | 1360 |
| "        | 31    | 22.3 | 20.0 | 57.2 | .2  | 1.0 | .4  | 84 | .032 | 1.9 | 1.50 | "    |
| "        | 32    | 21.9 | 19.3 | 57.5 | .2  | 1.0 | .4  | 88 | .019 | 1.1 | 1.66 | "    |
| "        | 33    | 21.6 | 19.0 | 58.1 | .2  | 1.0 | .4  | 85 | .012 | .7  | 1.83 | "    |

\* Parentheses around sinter numbers indicate analyses were calculated from batch compositions.

TABLE 7.—(Continued)

|          | SiO <sub>2</sub><br>% | Al <sub>2</sub> O <sub>3</sub><br>% | CaO<br>% | Fe <sub>2</sub> O <sub>3</sub><br>% | TiO <sub>2</sub><br>% | Total<br>Na <sub>2</sub> O K <sub>2</sub> O<br>and MgO | %Al <sub>2</sub> O <sub>3</sub><br>ex-<br>tracted | Wt. SiO <sub>2</sub><br>from 10<br>grams | 100 x SiO <sub>2</sub><br>SiO <sub>2</sub> +Al <sub>2</sub> O <sub>3</sub><br>in extract | Mole<br>Ratio<br>CaO/Al <sub>2</sub> O <sub>3</sub> | Sinter<br>Temp.<br>°C. |
|----------|-----------------------|-------------------------------------|----------|-------------------------------------|-----------------------|--|---|--|--|---|------------------------|
| "        | 21.3                  | 18.0                                | 59.8     | .2                                  | 1.2                   | .4   | 83  | .022                                     | 1.5  | 2.00  | 1360                   |
| "        | 21.8                  | 18.5                                | 57.7     | .3                                  | 1.2                   | .4   | 42  | .026                                     | 3.2  | 1.66  | 1320                   |
| "        | 21.8                  | 18.5                                | 57.7     | .3                                  | 1.2                   | .4   | 62  | .034                                     | 2.9  | 1.66  | 1340                   |
| "        | 21.8                  | 18.5                                | 57.7     | .3                                  | 1.2                   | .4   | 95  | .020                                     | 1.6  | 1.66  | 1380                   |
| "        | 21.8                  | 18.5                                | 57.0     | .2                                  | 1.2                   | .4   | 93  | .031                                     | 1.8  | 1.66  | 1400                   |
| Clay 874 | Ign.                  | 52.7                                | 0        | .4                                  | 2.5                   | .3   |   |  |  |   |                        |
| Sinter   | 77                    | 24.1                                | 55.0     | .2                                  | 1.1                   | .4   | 94  | .042                                     | 1.8  | 1.40  | 1360                   |
| "        | 40                    | 24.1                                | 55.3     | .2                                  | .8                    | .4   | 95  | .036                                     | 1.6  | 1.50  | "                      |
| "        | 41                    | 23.4                                | 56.5     | .2                                  | 1.0                   | .4   | 95  | .030                                     | 1.3  | 1.66  | "                      |
| "        | 42                    | 22.5                                | 57.4     | .2                                  | 1.0                   | .4   | 93  | .020                                     | .9   | 1.83  | "                      |
| "        | 133                   | 22.3                                | 58.2     | .2                                  | .8                    | .4   | 72  | .036                                     | 2.2  | 2.00  | "                      |
| "        | 163                   | 23.0                                | 56.2     | .2                                  | .9                    | .4   | 70  | .044                                     | 2.7  | 1.66  | 1320                   |
| "        | (212)                 | 22.9                                | 56.4     | .2                                  | 1.1                   | .4   | 85  | .038                                     | 1.9  | 1.66  | 1340                   |
| "        | 120                   | 23.4                                | 56.6     | .2                                  | .9                    | .4   | 95  | .026                                     | 1.2  | 1.66  | 1380                   |
| "        | 185                   | 22.2                                | 55.5     | .2                                  | 1.0                   | .4   | 94  | .034                                     | 1.4  | 1.66  | 1400                   |
| Clay 875 | Ign.                  | 62.6                                | 0        | 1.5                                 | 3.1                   | .6   |   |  |  |   |                        |
| Sinter   | 78                    | 30.7                                | 52.1     | .6                                  | 1.5                   | .5   | 88  | .034                                     | 1.2  | 1.40  | 1360                   |
| "        | 43                    | 30.6                                | 52.5     | .8                                  | 1.4                   | .5   | 95  | .036                                     | 1.2  | 1.50  | "                      |
| "        | 44                    | 28.6                                | 54.0     | .7                                  | 1.4                   | .5   | 96  | .035                                     | 1.3  | 1.66  | "                      |
| "        | 45                    | 28.7                                | 55.3     | .6                                  | 1.4                   | .5   | 88  | .024                                     | .9   | 1.83  | "                      |
| "        | 134                   | 29.2                                | 56.6     | .7                                  | 1.4                   | .5   | 78  | .030                                     | 1.3  | 2.00  | "                      |
| "        | 97                    | 29.7                                | 54.3     | .7                                  | 1.5                   | .5   | 57  | .042                                     | 2.4  | 1.66  | 1320                   |
| "        | 164                   | 29.5                                | 54.0     | .7                                  | 1.3                   | .5   | 93  | .032                                     | 1.2  | 1.66  | 1360                   |
| Clay 876 | Ign.                  | 38.3                                | .2       | 1.4                                 | 2.1                   | 1.3  |   |  |  |   |                        |
| Sinter   | 79                    | 16.6                                | 57.6     | .6                                  | .9                    | 1.0  | 88  | .028                                     | 1.9  | 1.40  | "                      |
| "        | 46                    | 16.4                                | 58.0     | .6                                  | .8                    | 1.0  | 93  | .028                                     | 1.8  | 1.50  | "                      |
| "        | 47                    | 16.2                                | 58.5     | .6                                  | .8                    | 1.0  | 91  | .022                                     | 1.5  | 1.66  | "                      |
| "        | 48                    | 15.3                                | 59.0     | .6                                  | .8                    | 1.0  | 92  | .009                                     | .6   | 1.83  | "                      |
| "        | 135                   | 15.3                                | 59.8     | .6                                  | .8                    | 1.0  | 80  | .023                                     | 1.9  | 2.00  | "                      |
| "        | 165                   | 16.5                                | 57.9     | .6                                  | .7                    | 1.0  | 63  | .027                                     | 2.5  | 1.66  | 1320                   |
| "        | (213)                 | 15.9                                | 58.3     | .6                                  | .9                    | 1.0  | 84  | .028                                     | 2.1  | 1.66  | 1340                   |
| "        | 121                   | 23.7                                | 58.7     | .6                                  | .7                    | 1.0  | 94  | .019                                     | 1.3  | 1.66  | 1380                   |
| "        | 186                   | 23.5                                | 58.5     | .6                                  | .8                    | 1.0  | 92  | .022                                     | 1.5  | 1.66  | 1400                   |



TABLE 7.—(Concluded)

|               | SiO <sub>2</sub><br>% | Al <sub>2</sub> O <sub>3</sub><br>% | CaO<br>% | Fe <sub>2</sub> O <sub>3</sub><br>% | TiO <sub>2</sub><br>% | Total<br>Na <sub>2</sub> O, K <sub>2</sub> O<br>and MgO | %Al <sub>2</sub> O <sub>3</sub><br>ex-<br>tracted | Wt. SiO <sub>2</sub><br>from 10<br>grams | $\frac{100 \times \text{SiO}_2}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$<br>in extract | Mole<br>Ratio<br>CaO/Al <sub>2</sub> O <sub>3</sub> | Sinter<br>Temp.<br>°C. |
|---------------|-----------------------|-------------------------------------|----------|-------------------------------------|-----------------------|---|---|--|--|---|------------------------|
| Clay 881..... | Ign.                  | 41.5                                | 0        | 1.7                                 | 2.2                   | 1.0   |   |  |  |   |                        |
| Sinter.....   | 85                    | 18.5                                | 56.9     | .8                                  | .8                    | .7  | 89  | .024                                     | 2.0  | 1.40  | 1360                   |
| ".....        | 64                    | 17.4                                | 58.3     | .8                                  | .9                    | .7  | 99  | .038                                     | 2.1  | 1.50  | "                      |
| ".....        | 65                    | 18.4                                | 58.2     | .8                                  | .9                    | .7  | 93  | .024                                     | 1.4  | 1.66  | "                      |
| ".....        | 66                    | 18.0                                | 59.0     | .8                                  | .9                    | .7  | 90  | .008                                     | .5   | 1.83  | "                      |
| ".....        | 137                   | 16.8                                | 59.4     | .7                                  | .7                    | .7  | 79  | .024                                     | 1.8  | 2.00  | "                      |
| ".....        | 198                   | 18.0                                | 58.2     | .8                                  | .8                    | .7  | 91  | .022                                     | 1.3  | 1.66  | "                      |
| ".....        | 176                   | 18.0                                | 57.5     | .7                                  | .7                    | .7  | 60  | .027                                     | 2.4  | 1.66  | 1320                   |
| ".....        | 141                   | 17.9                                | 58.0     | .8                                  | .9                    | .7  | 89  | .026                                     | 1.6  | 1.66  | 1340                   |
| ".....        | 144                   | 17.9                                | 58.4     | .8                                  | .8                    | .7  | 95  | .018                                     | 1.0  | 1.66  | 1380                   |
| ".....        | (191)*                | 17.5                                | 57.8     | .8                                  | .9                    | .7  | 93  | .026                                     | 1.6  | 1.66  | 1400                   |
| Clay 883..... | Ign.                  | 39.4                                | .1       | .5                                  | 3.5                   | .5  |   |  |  |   |                        |
| Sinter.....   | 145                   | 17.2                                | 57.7     | .3                                  | 1.4                   | .5  | 80  | .032                                     | 2.3  | 1.40  | 1360                   |
| ".....        | 146                   | 16.7                                | 58.4     | .2                                  | 1.5                   | .5  | 86  | .032                                     | 2.2  | 1.50  | "                      |
| ".....        | 147                   | 16.9                                | 58.6     | .3                                  | 1.3                   | .5  | 83  | .028                                     | 1.9  | 1.66  | "                      |
| ".....        | 148                   | 16.3                                | 59.6     | .2                                  | 1.4                   | .5  | 85  | .022                                     | 1.6  | 1.83  | "                      |
| ".....        | 149                   | 16.2                                | 59.4     | .2                                  | 1.2                   | .5  | 74  | .022                                     | 1.8  | 2.00  | "                      |
| ".....        | (177)                 | 16.4                                | 58.2     | .3                                  | 1.4                   | .5  | Did not dust                                      |  |  |   | 1320                   |
| ".....        | (205)                 | 16.4                                | 58.2     | .3                                  | 1.4                   | .5  | 52  | .023                                     | 2.6  | 1.66  | 1340                   |
| ".....        | (206)                 | 16.4                                | 58.2     | .3                                  | 1.4                   | .5  | 84  | .028                                     | 2.0  | 1.66  | 1380                   |
| ".....        | (192)                 | 16.4                                | 58.2     | .3                                  | 1.4                   | .5  | 82  | .030                                     | 2.2  | 1.66  | 1400                   |

\* Parentheses around sinter numbers indicate analyses were calculated from batch compositions.

EFFECT OF TIME HELD AT SINTERING  
TEMPERATURE

A number of sinters were prepared using selected clay samples for which the time that the sinter was held at maximum temperature was varied. For all of these sinters, the lime-alumina ratio was 1.66 and the temperature was 1360°C. The data are recorded in table 8.

Kaolinite clay sinters all showed reduced extractability when the time held at 1360°C. was only 10 minutes, but there appeared to be no advantage in heating them for periods greater than one hour.

Halloysite clay sinters showed better extractability with increasing time. This clay is not well suited to treatment by the lime-sinter process. The highest temperature used and the longest heating periods were insufficient to give good yields from sinters made with this clay.

The extractability of the gibbsite-kaolinite clay was not affected by variations in the sinter time within the range of times used.

The montmorillonite clay and the illite clay (sample 870) appeared to be rather critically sensitive to overtime heating. The reason for the bad effect of long time and high temperature heating is probably related

TABLE 8.—THE EFFECT OF TIME HELD AT SINTERING TEMPERATURE

| Sinter No. | Time at 1360°C. in minutes | Al <sub>2</sub> O <sub>3</sub> extracted in percent | Clay Sample No. | Type of clay                             |
|------------|----------------------------|---|-----------------|--|
| 201.....   | 10                         | 32  | 865             | kaolinite                                |
| 12.....    | 60                         | 88  |                 |  |
| 225.....   | 240                        | 90  |                 |  |
| 290.....   | 10                         | 77  | 866             | illite,<br>kaolinite                     |
| 288.....   | 60                         | 78  |                 |  |
| 291.....   | 240                        | 79  |                 |  |
| 22.....    | 60                         | 45  | 867             | halloysite                               |
| 203.....   | 120                        | 61  |                 |  |
| 233.....   | 240                        | 70  |                 |  |
| 216.....   | 10                         | 61  | 868             | montmorillonite                          |
| 19.....    | 60                         | 87  |                 |  |
| 295.....   | 150                        | 67  |                 |  |
| 234.....   | 240                        | 56  |                 |  |
| 217.....   | 10                         | 57  | 869             | kaolinite                                |
| 56.....    | 60                         | 88  |                 |  |
| 226.....   | 240                        | 90  |                 |  |
| 218.....   | 10                         | 72  | 870             | high iron illite                         |
| 26.....    | 60                         | 71  |                 |  |
| 227.....   | 240                        | 59  |                 |  |
| 219.....   | 10                         | 32  | 873             | kaolinite<br>(flint clay)                |
| 32.....    | 60                         | 88  |                 |  |
| 228.....   | 240                        | 93  |                 |  |
| 296.....   | 10                         | 92  | 874             | gibbsite, kaolinite<br>(bauxitic kaolin) |
| 41.....    | 60                         | 95  |                 |  |
| 299.....   | 240                        | 92  |                 |  |
| 221.....   | 10                         | 49  | 876             | kaolinite                                |
| 47.....    | 60                         | 91  |                 |  |
| 230.....   | 240                        | 92  |                 |  |
| 222.....   | 10                         | 45  | 879             | kaolinite<br>(ball clay)                 |
| 59.....    | 60                         | 91  |                 |  |
| 231.....   | 240                        | 90  |                 |  |
| 202.....   | 10                         | 46  | 881             | kaolinite                                |
| 65.....    | 60                         | 93  |                 |  |
| 232.....   | 240                        | 93  |                 |  |

to the relatively high content of alkali in both clays. Although the alkali would tend to be lost by vaporization from the sinter at high temperatures and with prolonged heating periods, its presence no doubt indirectly inhibits inversion of dicalcium silicate by causing the formation of appreciable amounts of stable glass. The other illite clay (sample 866) did not show this sensitivity to sintering time. The reason for the different behavior of this illite clay is obscure although it may be because it contains an appreciable amount of kaolinite and considerably less iron than sample 870.

#### EFFECT OF FURNACE ATMOSPHERE

In a great many tests made by the writers and also by others, the briquetted sinter mixes were placed upon a graphite block because graphite is the only material so far

found to which the sintered briquets do not stick. It was noted on many occasions that the end of the briquet which was adjacent to the graphite block was different in color from the opposite end and that the color changed more or less gradually as the distance from the graphite increased. Furthermore, it was noticed that in some cases there was a pronounced odor of hydrogen sulfide when the sodium carbonate extracts were acidified in preparing to determine their alumina content. When the iron content of the sinters was considerable, the sintered material usually showed a gain in weight when ignited in oxidizing atmospheres if the briquet was sintered on a graphite block. All of these phenomena indicated that more or less reduction was taking place during the sintering process. It was therefore decided to determine, if

TABLE 9.—THE EFFECT OF FURNACE ATMOSPHERE ON EXTRACTABILITY

| Clay Sample No.                               | CaO/Al <sub>2</sub> O <sub>3</sub> Mole Ratio | Atmosphere |                   |             |
|---|---|------------|-------------------|-------------|
|   |   | Oxidizing  | Reducing          |             |
|   |   |            | Graphite Crucible | Natural Gas |
| Alumina extracted in percent                  |   |            |                   |             |
| 865<br>kaolinite                              | 1.35  | 83         | 83                | 83          |
|   | 1.50  | 92         | 89                | 93          |
|   | 1.66  | 88         | 89                | 71          |
|   | 1.83  | 84         | 92                | 88          |
| 866<br>illite                                 | 1.40  | 63         | 59                | 59          |
|   | 1.50  | 78         | 67                | 64          |
|   | 1.66  | 81         | 77                | 71          |
|   | 1.83  | 77         | 76                | 78          |
| 868<br>montmorillonite                        | 1.40  | 83         | 70                | 77          |
|   | 1.50  | 77         | 80                | 77          |
|   | 1.66  | 87         | 86                | —           |
|   | 1.83  | —          | 84                | 84          |
| 870<br>illite                                 | 1.40  | 58         | 63                | 67          |
|   | 1.50  | 57         | 69                | 72          |
|   | 1.66  | 71         | 81                | 81          |
|   | 1.83  | 69         | 82                | 83          |
| 871<br>kaolinite<br>illite<br>montmorillonite | 1.40  | 73         | 62                | 85          |
|   | 1.50  | 80         | 73                | 81          |
|   | 1.66  | 85         | 79                | 70          |
|   | 1.83  | 83         | 64                | 58          |

possible, whether furnace atmosphere exerted any considerable influence on the amount of extractable alumina. Tests were made with five different clays.

Oxidizing atmospheres were maintained by placing the briquets in an electrically heated muffle furnace which contained no combustible material whatever. Reducing atmospheres were maintained in two ways: (1) the briquets were sintered in covered graphite crucibles; (2) the briquets were placed in the furnace on a graphite block and a slow current of natural gas was passed into the furnace during the sintering period. The sintering temperature was 1360° in all cases.

The clays chosen for test were numbers 865, 866, 868, 870, and 871. Sinters with lime-to-alumina ratios varying from 1.4 to 1.83 were made with each of the five clays using oxidizing atmospheres and also reducing atmospheres. The extraction data are presented in table 9.

With clay 865 (kaolinite) there was no significant difference in the amount of alumina extracted which could be correlated with furnace atmosphere. With clay 871 (kaolinite, illite, and a little montmorillonite), which was chosen because it contained considerable iron, the data are erratic. The high-lime sinters gave less satisfactory yields in reducing atmospheres.

Sinters made from clay 866 (largely illite high in iron) gave slightly better extraction in oxidizing atmosphere when the lime-to-alumina ratio was low, but there was no significant difference when higher lime-to-alumina ratios were used. Sintners prepared from clay 870 (illite clay very high in iron) gave definitely better yields of alumina from sintners burned in reducing atmospheres.

There were no significant differences in alumina yields from sintners prepared from clay 868 (montmorillonite) which could be correlated with atmosphere.

#### DUSTING OF SINTERS

The speed of dusting is erratic even for sintners made with the same type of clay and fired to the same temperature. The completeness of dusting is occasionally erratic

especially for sintners made with clays containing alkalis and/or considerable iron. High temperatures and long heating periods favor rapid and complete dusting. However, it was only at the highest temperature (1400°C.) used that the dusting was noticeably faster. The average dusting time for sintners heated to 1360°, 1340° and 1320°C. was nearly the same for the same type clays. There were some sintners prepared at all of these temperatures which required several days to dust.

Sinters prepared with kaolinite clays usually dust fairly completely in 5 to 15 minutes. None of the sintners prepared with kaolinite clays 869, 871, 873, 876, 878, 879, 880, and 881 required more than 30 minutes to dust. A few sintners prepared with kaolinite clays 865 and 877 required from 2 hours to overnight to dust. Only one sinter prepared from a kaolinite clay and sintered at a temperature of 1320° or above did not dust at all.

The dusting characteristics of sintners prepared with gibbsite-kaolinite clays were much like those of sintners prepared with kaolinite clays. Sintners prepared from halloysite clay 867 dusted quickly but contained considerable gritty material. Sintners prepared with illite and montmorillonite clay frequently dusted slowly and incompletely.

Although it is usually true that quick dusting sintners are apt to extract well, they do not always do so. For example, sinter 16 from clay 866 was incompletely dusted after standing overnight yet yielded 81 percent of its alumina. Sinter 194 from the same clay dusted completely in 10 minutes and yielded 77 percent of its alumina. Another sinter from this same clay dusted in 4 minutes but yielded only 50 percent of its alumina. Examples of less extreme variation with all types of clay are common. In some instances the explanation is obvious. The dusting may be quick but incomplete. In other instances there seems to be no obvious reason why one sinter dusts in 10 minutes and another requires 24 hours although both give good extraction yields. In some cases dusting time is related to the presence of iron or magnesia, as described on pages 32, 33.

As might be expected, gritty particles in the sinter dust are not associated with the best yields of extractable alumina. Such particles are sometimes glassy and sometimes resemble particles of burnt clay, suggesting that the clay and lime have not always been sufficiently mixed, even though all batches were tumbled for several hours in mixing jars, and in most cases were sieved afterward.

#### SILICA IN THE ALUMINA EXTRACT

Under the extraction conditions which prevailed in these studies, sinters from kaolinite clays gave alumina extracts in which the average values of the ratio  $(100 \times \text{SiO}_2) / (\text{Al}_2\text{O}_3 + \text{SiO}_2)$  usually ranged from 1.5 to 1.7. The weight of silica extracted from 10 grams of sinter averaged from 0.02 to 0.03 gram. High sintering temperatures resulted in lowered solubility of silica, and low temperatures favored increased solubility of silica. The amount of soluble silica decreased with increasing lime-to-alumina ratio, except that some sinters appeared to have more soluble silica when the  $\text{CaO}/\text{Al}_2\text{O}_3$  ratio was increased beyond 1.83.

Sinters made with gibbsite-kaolinite clay behaved like those made with kaolinite clays, so far as silica extraction was concerned, except that the lime-to-alumina ratio did not clearly affect the amount of soluble silica.

Sinters prepared with illite and with montmorillonite clays gave extracts in which the value of the ratio  $(100 \times \text{SiO}_2) / (\text{Al}_2\text{O}_3 + \text{SiO}_2)$  was 2.0 to 2.5. This high value is the result of low soluble alumina rather than high soluble silica. The average weight of silica extracted from 10 grams of sinter was only 0.015 gram. The response to changes in lime-to-alumina ratio was similar to that noted for kaolinite clays. It could not be observed that the amount of soluble silica varied with sinter temperature.

Extracts from sinters prepared with the halloysite clay had about the same soluble silica content as those prepared with kaolins. There was no definite variation of soluble silica with either temperature or lime-alumina ratio.

## EFFECT OF MINOR COMPONENTS PRESENT IN THE RAW MATERIALS

### GENERAL COMMENTS

All clays and limestones likely to be chosen as raw materials for the lime-sinter process are apt to contain magnesia, sulfur, phosphorous, and iron in varying quantities. It was decided, therefore, to make some tests for the purpose of determining whether these elements are likely to exert any important influence on the efficiency of the extraction. The study was limited to one kaolinite clay. Only in a pure mono-mineral clay could the effects be easily detected. Clay 877 was chosen because it was the purest and cleanest kaolinite clay available.

Sinter mixes were prepared using precipitated calcium carbonate as a source of lime. The mole ratio of lime-to-alumina was 1.66 in all test batches. Quantities of iron, sulfur, phosphorous and magnesia were added to these batches in the form of  $\text{Fe}_2\text{O}_3$  (rouge),  $\text{CaSO}_4$  (precipitated),  $\text{Ca}_3(\text{PO}_4)_2$  (precipitated) and  $\text{MgCO}_3$  (precipitated), and in amounts calculated to cover the ranges most likely to be encountered in practice. The batches were briquetted and sintered for one hour at  $1360^\circ\text{C}$ . (except as otherwise noted below).

### EFFECT OF MAGNESIUM

Other workers<sup>3</sup> have reported the adverse effect of  $\text{MgO}$  on the amount of extractable alumina in lime-clay sinters. Since  $\text{MgO}$  is a common impurity in both the limestone and clays likely to be used in the lime-sinter process, it was given more attention than the other minor components.

Precipitated magnesium carbonate was added to the sinter mixes in such quantities that the amount of  $\text{MgO}$  (calculated) varied from about 1.5 percent to about 37 percent of the weight of  $\text{Al}_2\text{O}_3$  in the finished sinter. One series was sintered at  $1360^\circ$  and another at  $1400^\circ\text{C}$ ., both for one hour. The results are shown graphically in figure 3, which gives percent of alumina extracted as a function of the ratio  $\text{MgO}/\text{Al}_2\text{O}_3$  expressed as weight percent. One sinter not shown on the figure contained  $\text{MgO}$

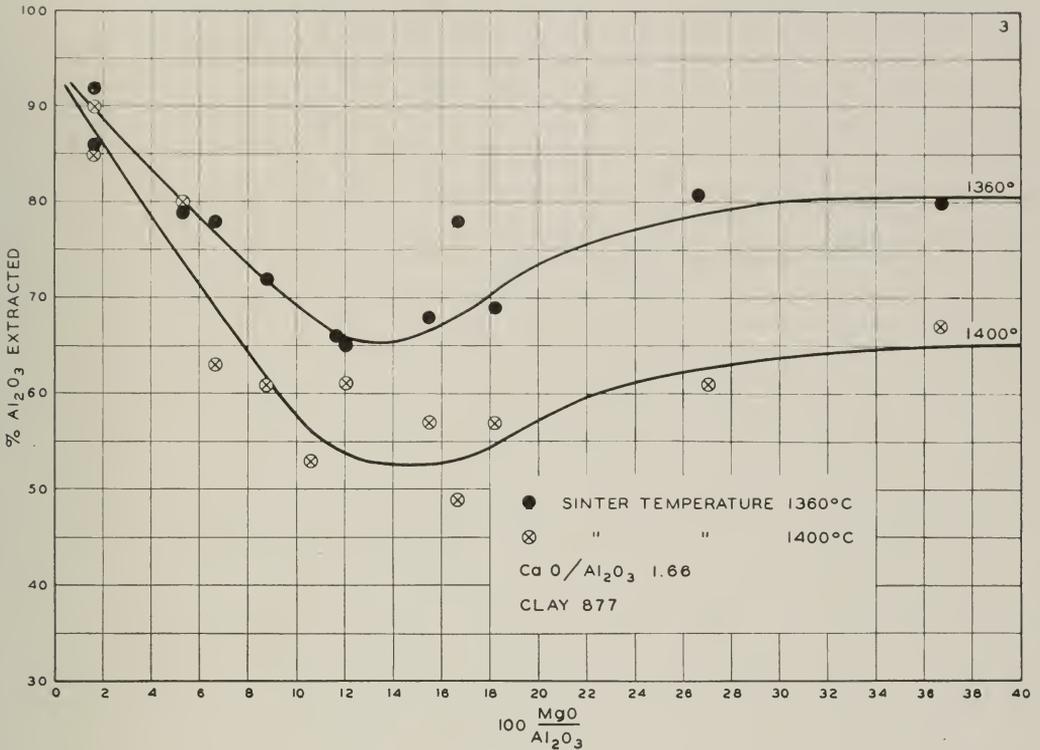


FIG. 3.—Percent Al<sub>2</sub>O<sub>3</sub> extracted versus  $100 \frac{\text{MgO}}{\text{Al}_2\text{O}_3}$  in sinter mix.

equal to 242 percent of the weight of alumina. This sinter was made at 1400°C. Sixty-three percent of the alumina it contained was extracted.

The data show that the alumina yield decreased as the MgO increased up to about 14 percent MgO. With further increases in MgO the yield increased until about 28 percent MgO was present. Larger amounts of MgO caused no further change in alumina yield. The scattering of points about the 1400°C. curve on figure 3 is due in part to the fact that it was necessary to make two heats in collecting the data for this curve. If the data from each heat are considered separately, there is much less scattering of the points. This suggests that some phenomena which is very sensitive to slight changes in conditions may be involved.

It is of interest to note that the effect of MgO on the extractability was greater at the higher temperature. This suggests that the phenomenon may be related to the solu-

bility of periclase in the liquid portion of the sinter. Presumably, there is more liquid in the 1400°C. sinter and hence more dissolved MgO. Possibly one reason why more Al<sub>2</sub>O<sub>3</sub> is extractable in the presence of excess MgO than in the presence of smaller quantities is that this excess MgO inhibits supersaturation of the liquid part of the sinter with MgO. This would mean that the saturation point is reached near the minimum on the curve where the MgO is about 14 percent of the alumina present. Reports of the optical examinations, however, note the presence of periclase in sinters on both sides of the minima. This would not rule out the supersaturation hypothesis, however, unless equilibrium conditions prevailed, and it is most unlikely that complete equilibrium was reached in these sinters. Reports of the X-ray examinations indicate the presence of an unidentified compound in some but not in all of these sinters. At 1360°C. approximately 65 percent of the

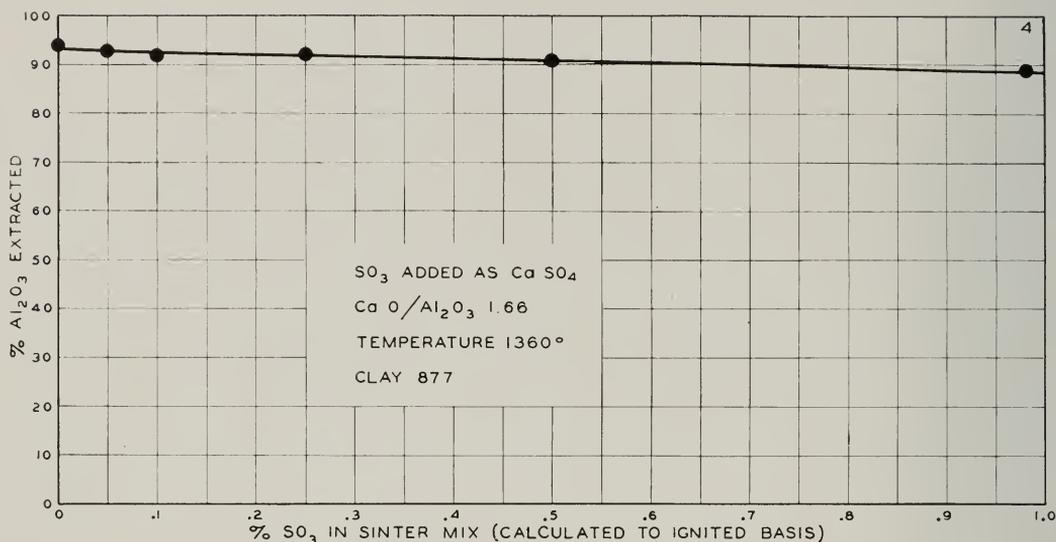


FIG. 4.—Percent  $\text{Al}_2\text{O}_3$  extracted versus percent  $\text{SO}_3$  in sinter mix.

alumina is extractable in the neighborhood of the minimum. The unextractable alumina and the  $\text{MgO}$  present are, therefore, in the proper proportions to form the spinel  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  on that part of the  $1360^\circ\text{C}$ . curve to the left of the minimum.

However, if the formation of  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  was the whole explanation, we should not expect the extractability to improve when further  $\text{MgO}$  is added nor should we expect the increased temperature to affect the extractability so markedly, although the increased temperature might promote solution of alumina in  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ , and explain the portion of the curves to the left of the minima. Similar objections might be raised to any explanation based on the hypothesis of a phase composed of any compound involving aluminum and magnesium oxides.

Whatever the explanation of the peculiar behavior of sinters containing magnesium, it seems clear that the presence of magnesium in the quantities most likely to be encountered is bad and that its effect is aggravated at higher temperatures.

It was observed in the course of this series of tests that when a group of sinters was prepared under precisely identical conditions, increasing the quantity of magnesia shortened the time required for the sintered briquet to "dust."

#### EFFECT OF SULFUR

Precipitated calcium sulfate was added to the mixtures to produce sinters containing up to one percent of sulfur as  $\text{SO}_3$ . The six sinters prepared gave yields of extractable alumina which were the same within the precision of the work. Sulfur added as calcium sulfate apparently has little or no harmful effect. The test data are presented in figure 4.

#### EFFECT OF PHOSPHORUS

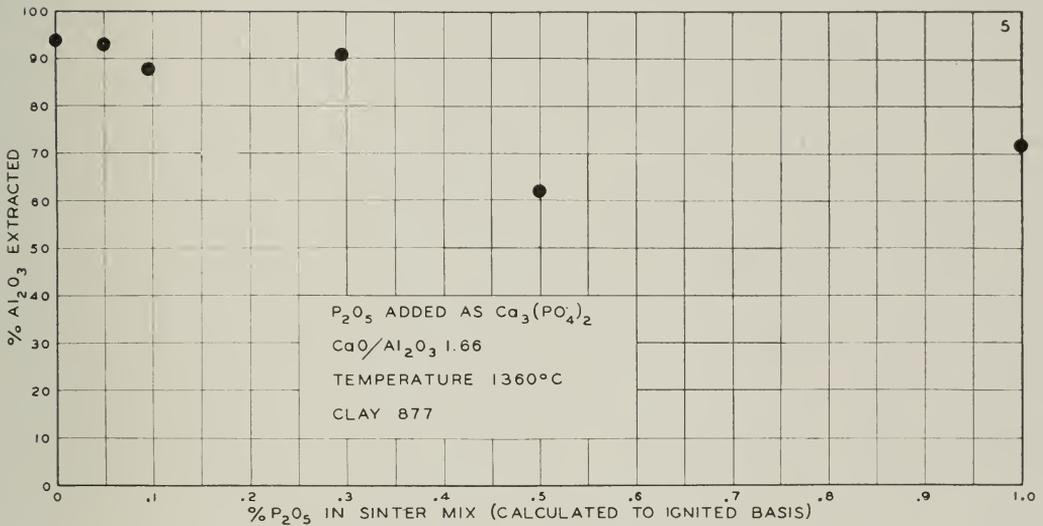
Phosphorus is present as an impurity in many limestones and in some clays, and because it has been reported<sup>4,5</sup> to inhibit the transformation of  $\beta\text{-C}_2\text{S}$  to the  $\gamma$ -form, it was desirable to obtain some information concerning its influence on the lime-sinter process.

Six sinters were made with added  $\text{Ca}_3(\text{PO}_4)_2$ . The  $\text{P}_2\text{O}_5$  content of the sinters (ignited basis) varied from zero to one percent by weight. The results presented in table 10 and figure 5 show that the extractability falls off as the phosphorus in the sinter increases.

The effect of phosphorus was worse than the numerical data indicate. Sinter 312 was very poorly dusted and contained much coarse sandy material. Sinter 313 was a hard glasslike lump that showed no evidence

TABLE 10.—THE EFFECT OF PHOSPHORUS ON THE EXTRACTABILITY OF LIME-CLAY SINTERS

| Sinter No. | % P <sub>2</sub> O <sub>5</sub> in Sinter | % Al <sub>2</sub> O <sub>3</sub> Extracted | Sinter Temp. | Dusting Time |
|------------|---|--|--------------|--------------|
| 303        | .01                                       | 94   | 1360         | 1.5 hours    |
| 309        | .05                                       | 93   | 1360         | 1.5 hours    |
| 310        | .10                                       | 88   | 1360         | overnight    |
| 311        | .29                                       | 91   | 1360         | overnight    |
| 312        | .49                                       | 62   | 1360         | several days |
| 313        | 1.00                                      | 72   | 1360         | did not dust |

FIG. 5.—Percent Al<sub>2</sub>O<sub>3</sub> extracted versus percent P<sub>2</sub>O<sub>5</sub> in sinter mix.

of dusting after several days. It was necessary to crush and grind it through a 200-mesh sieve before it could be extracted at all. The tests indicate that no limestone containing phosphorus should be used as raw material in the lime-sinter process without very careful testing.

#### EFFECT OF IRON

The amount of iron present in good kaolinite clays usually does not exceed one or two percent as Fe<sub>2</sub>O<sub>3</sub>, but may run much higher in other clays and shales. Examination of figure 6 indicates that the effect of iron in the form added is not serious unless the quantity present in the sinter is greater than two or three percent. The optical examination usually shows the presence of

the compound 4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub> in clay-lime sinters which contain appreciable quantities of iron. This compound does not easily yield its alumina to dilute sodium carbonate solutions so that it is not surprising that iron reduces the yield of alumina from clay-lime sinters. The reduction in yield appears to be somewhat greater than is accounted for by the quantity of alumina involved in tetra-calcium-alumino-ferrite. The difference may be partly due to the fact that considerable lime is also tied up in the compound. This, of course, would have the effect of changing the lime-alumina ratio.

It was observed that increasing the iron accelerated the dusting rate when conditions under which the sinters were produced were otherwise identical.

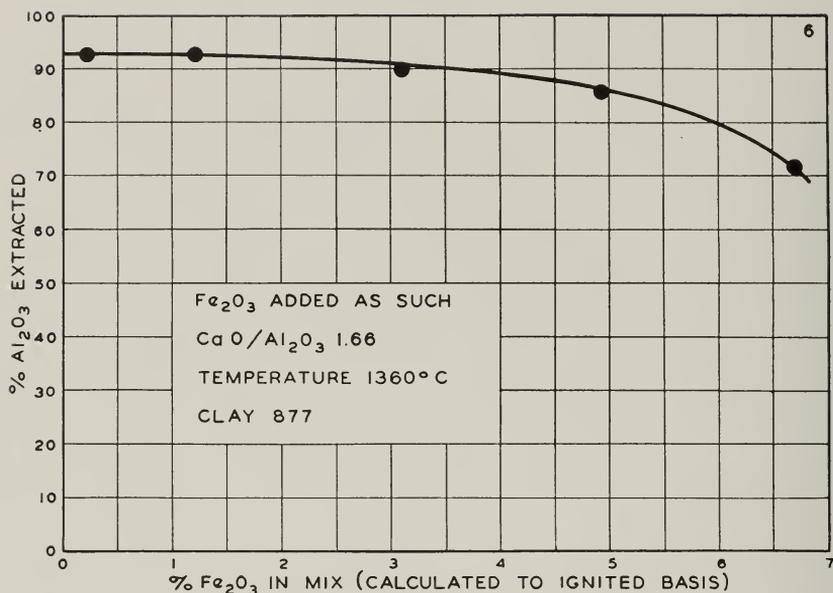


FIG. 6.—Percent  $\text{Al}_2\text{O}_3$  extracted versus percent  $\text{Fe}_2\text{O}_3$  in sinter mix.

#### EFFECT OF DIFFERENT TYPES OF LIMESTONE

Varying results have been reported<sup>3</sup> when different limestones were used as sources of lime in the lime-sinter process. It was thought that the differences might be due to the size of the ultimate crystals of calcite of which the limestone is composed. Accordingly, three samples of limestone were selected which are designated R7, R2, and MC. R7 is fine-grained, R2 is intermediate-grained, and MC is coarse-grained. R7 and R2 were from the St. Louis limestone taken from a quarry near Alton, Illinois. MC was from the Burlington limestone taken from a quarry near Marblehead, Illinois. The analyses of the limestones are given in table 5 on page 13.

The limestones were ground so that 95 percent passed through a 200-mesh sieve. Sinters were prepared using illite clay 870 and kaolinite clays 877 and 880. The lime-alumina ratio chosen was 1.50. This low ratio was selected so that small or moderate effects would not be obscured by the presence of excess lime. The sinters were burned at  $1360^\circ\text{C}$ . for one hour following which they were extracted in the usual manner.

The results presented in table 11 indicate no basis of choice between the three limestones. For a given clay any one of the limestones or a precipitated calcium carbonate which is extremely fine-grained gives equally good results within experimental error. The sinters all dusted well and within a reasonable time.

It must be concluded that differences in limestone insofar as they affect the efficiency of the lime-clay-sinter process are due to factors other than the grain size.

TABLE 11.—EFFECT OF DIFFERENT TYPES OF LIMESTONE ON EXTRACTABILITY OF CLAY-LIME SINTERS

| Clay Sample No.  | Limestone Sample No. | Sinter No. | Percent $\text{Al}_2\text{O}_3$ extracted |
|------------------|----------------------|------------|---|
| 870<br>illite    | R2                   | 314        | 58  |
|                  | R7                   | 315        | 59  |
|                  | MC                   | 316        | 54  |
| 877<br>kaolinite | Ppt $\text{CaCO}_3$  | 25         | 57  |
|                  | R2                   | 317        | 92  |
|                  | R7                   | 318        | 88  |
|                  | MC                   | 319        | 90  |
|                  | Ppt $\text{CaCO}_3$  | 49         | 93  |
| 880<br>kaolinite | R2                   | 320        | 91  |
|                  | R7                   | 339        | 86  |
|                  | MC                   | 340        | 89  |
|                  | Ppt $\text{CaCO}_3$  | 61         | 93  |

## MINERALOGICAL ANALYSES OF SINTERS

### MICROSCOPIC ANALYSIS

Microscopic studies were made with the petrographic microscope on mounts prepared by immersing the sinter material in liquids of known refractive index. Magnifications up to  $900\times$  were used.

### GENERAL COMMENTS

The principal phases developed in the sinters were  $C_2S(2CaO.SiO_2)$  and  $C_3A_3(5CaO.3Al_2O_3)$ . The former was present in euhedral grains and the latter as interstitial material between grains. In some sinters prepared with high alumina (gibbsite-kaolinite) clays, a small amount of euhedral  $C_3A_3$  could be identified.

In sinters prepared with kaolinite clays the  $C_2S$  was usually in grains 5 to 10 microns in diameter (fig. 7B). The  $C_2S$  tended to be smaller in sinters prepared with clays composed of well crystallized kaolinite than in those prepared with clays composed of poorly crystallized kaolinite. In sinters prepared from clays composed of other clay minerals the same component was frequently 20 to 60 microns in diameter (fig. 7A).

The  $C_2S$  was usually in the  $\gamma$ -form although sinters prepared from all clay samples contain some uninverted  $\beta$ - $C_2S$ .

Sinters prepared from all types of clay contained a yellow-brown pigmentary material that was present usually in particles less than 2 microns in diameter. It was impossible to be certain of the identification of all of the pigmentary material, but a considerable part at least was  $4CaO.Al_2O_3.Fe_2O_3$ . The amount of this material was small in sinters prepared with halloysite or kaolinite clays because such clay minerals, unlike illite and montmorillonite, do not have appreciable amounts of iron in their lattice structure.

Sinters prepared with some clays at low temperatures contained some material that showed little or no development of the new phases. This material was isotropic in appearance which suggests that the reaction

of the components had not been carried to completion.

### EFFECT OF VARIATIONS IN LIME CONTENT IN SINTERS FIRED ONE HOUR AT 1360°C.

*Kaolinite clays.*—The inversion of  $C_2S$  to the  $\gamma$ -phase was most complete ( $90\% \pm$ ) in sinters with a lime-to-alumina ratio of 1.83. Sintere prepared with a lime-to-alumina ratio less than 1.66 frequently contained small amounts of CA — the amount increasing as the ratio decreased below 1.66. A component identified as  $C_3A$  was present in small amounts in sinters with a lime-to-alumina ratio of 1.83.

In general the amount of  $C_3A_3$  was about the same in sinters prepared with lime-to-alumina ratios of 1.66 and 1.83. The amount of this component decreased as the ratio decreased below 1.66.

The amount of pigmentary material increased as the lime content decreased.

*Illite and montmorillonite clays.*—Sinters prepared with such clays showed about the same general effects of changes in lime content as those prepared with kaolinite clay except that they had less tendency to develop CA or  $C_3A$ . Also the variation in the amount of inversion of  $C_2S$  to the  $\gamma$ -phase with changes in the lime content was greater for illite and montmorillonite clays than for kaolinite clays. Sintere of the former type clay with high or low lime content frequently contained as much as 70 percent  $\beta$ - $C_2S$ .

*Diaspore clays.*—Sintere prepared with a lime-to-alumina ratio of 1.66 were composed largely of  $C_3A_3$ . A small amount ( $25\% \pm$ ) of indistinct material, which may be incompletely reacted, was present also. Sintere with a lime-to-alumina ratio of 1.83 seemed to be about the same as the foregoing, but the indistinct material became more prominent as the lime-to-alumina ratio decreased below 1.66.

*Gibbsite-kaolinite clays.*—Sintere prepared with varying lime-to-alumina ratios up to 1.83 all appeared about the same, being composed almost wholly of  $C_2S$  and  $C_3A_3$ . Sintere with a higher ratio were somewhat different because of the presence of indis-

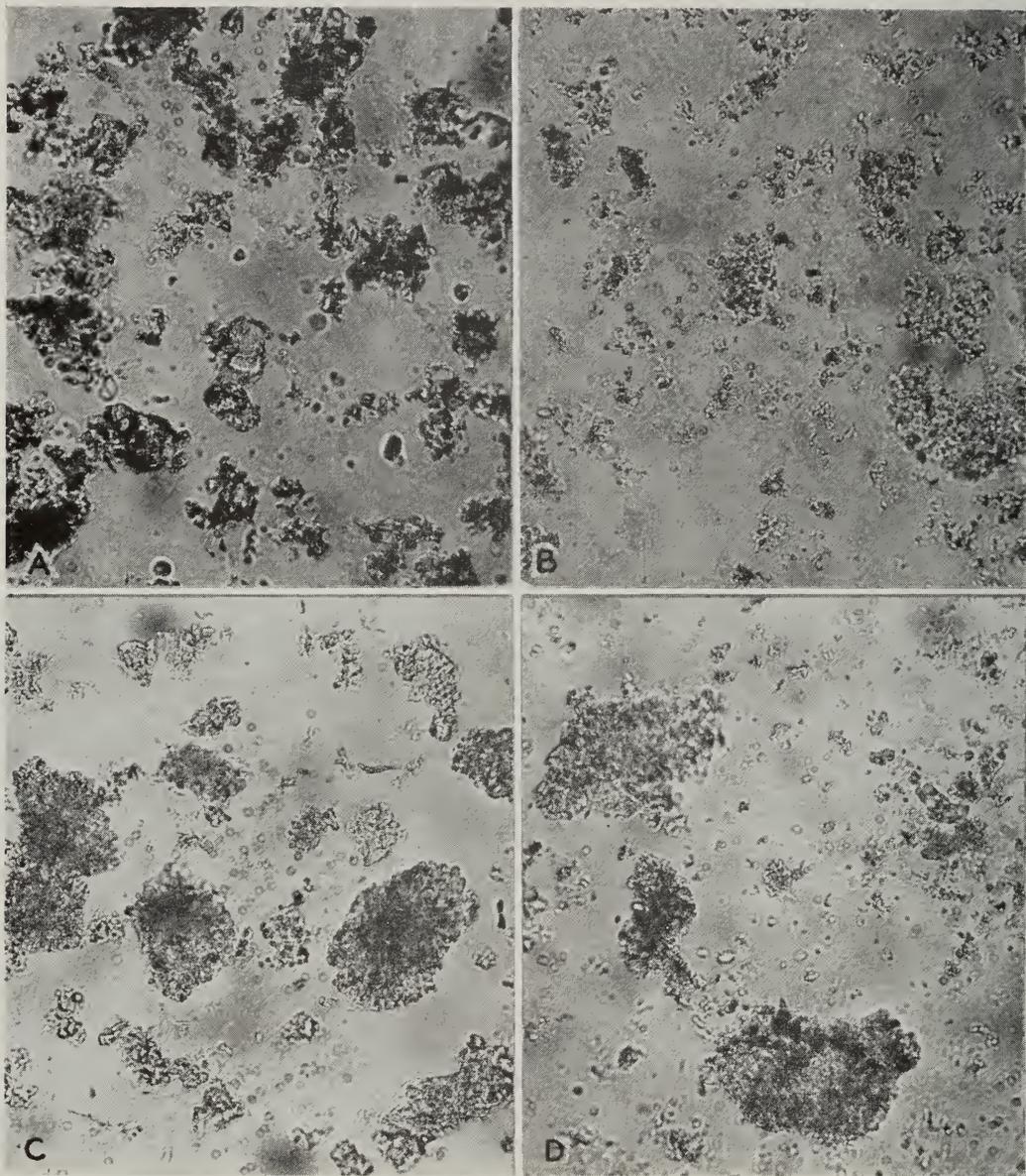


FIG. 7.—Photomicrographs of lime-clay sinters, 300X.

- A. Illite-clay sinter fired to 1360° C., showing distinct development of large particles of  $\gamma\text{C}_2\text{S}$ , and pigmentary ferrite (dark material).
- B. Kaolinite-clay sinter fired to 1360° C. showing distinct development of small particles of  $\gamma\text{C}_2\text{S}$ . The  $\text{C}_3\text{A}_2$  is interstitial between the silicate grains and is not evident on the photomicrograph.
- C. Halloysite-clay sinter fired to 1360° C. showing the development of some  $\text{C}_2\text{S}$ , and large aggregate masses of material that appear to be incompletely reacted.
- D. Kaolinite-clay sinter fired to 1320° C. showing the distinct development of small particles of  $\text{C}_2\text{S}$ , and large aggregate masses in which the new phases are less clearly developed than in B.

tinct material which seemed to be incompletely reacted.

*Halloysite clay.*—All sinters fired at 1360°C. contained a large amount (40% ±) of material which appeared to be incompletely reacted.

EFFECT OF VARIATIONS IN SINTERING TEMPERATURE ON BATCHES WITH A LIME-TO-ALUMINA RATIO OF 1.66 AND HELD AT SINTERING TEMPERATURE FOR ONE HOUR

*Kaolinite clay.*—Sinters fired at 1320°C. contained a considerable amount of material (40% ±) that suggested poor development of new phases (fig. 7D). The amount of this material decreased as the temperature increased until in sinters fired at 1360°C. almost the entire mass was composed of rather distinct new components, i.e., C<sub>2</sub>S and C<sub>3</sub>A<sub>3</sub>.

An increase in sintering temperature was accompanied by an increase in size of the  $\gamma$ -C<sub>2</sub>S grains from 5 to about 15 microns and a decrease in the amount of  $\beta$ -C<sub>2</sub>S. Inversion of C<sub>2</sub>S to the  $\gamma$ -phase was about complete in sinters prepared at 1400°C.

*Illite and montmorillonite clays.*—Sinters fired at 1320°C. were composed entirely of new reaction products. As the sintering temperature increased the size of the individual units of  $\gamma$ -C<sub>2</sub>S increased from about 20 to 60 microns, and the amount of  $\beta$ -C<sub>2</sub>S decreased slightly. The presence of illite or montmorillonite in kaolinite clays lowered the temperature required for complete reaction and increased the size of the C<sub>2</sub>S formed at a given temperature.

*Diaspore clay.*—Sinters fired at 1320°C. like those fired at 1360°C. were composed of C<sub>3</sub>A<sub>3</sub> with a relatively small amount (25% ±) of indistinct material that could not be positively identified.

*Gibbsite-kaolinite clay.*—Sinters made from clays of this type reacted to variation of sintering temperature in much the same manner as did those made from kaolinite clays except that the new phases showed slightly better development at 1320°C. and 1340°C.

*Halloysite clay.*—Sinters fired at 1360°C. were composed of about 50 percent of isotropic material that suggested incomplete reaction between components (fig. 7C). The remaining 50 percent was C<sub>2</sub>S and C<sub>3</sub>A<sub>3</sub>. About 20 percent of the sinter had the appearance of incomplete reaction after firing to 1400°C. and only after firing to 1450°C. were the phases about completely developed. The presence of halloysite in a clay would increase the necessary sintering temperature.

EFFECT OF VARIATIONS IN SINTERING TIME OF BATCHES WITH A LIME-TO-ALUMINA RATIO OF 1.66 FIRED AT 1360°C.

*Kaolinite clays.*—Sinters held at 1360°C. for only ten minutes contained a considerable amount (40% ±) of material showing poor development of new phases. The remaining 60 percent was made up of distinct particles of C<sub>2</sub>S and interstitial C<sub>3</sub>A<sub>3</sub>.

Sinters held at 1360°C. for one hour were composed almost completely of new phases, and those fired four hours at 1360°C. differed from the one-hour sinters only in having more complete inversion of the C<sub>2</sub>S to the  $\gamma$ -form and slightly larger individual units of C<sub>2</sub>S.

*Illite and montmorillonite clays.*—Sinters fired for ten minutes and 60 minutes at 1360°C., both showed nearly complete development of new phases.

*Gibbsite-kaolinite clays.*—Aggregates of isotropic material without the distinct development of new phases entirely composed sinters fired for only 10 minutes. Curiously the sinter of this clay (unlike those of the kaolinite clays) fired for 10 minutes, gave high extraction yields. Sintors fired one hour and four hours were both completely composed of new phases—the four-hour sinter contains a much larger portion of the C<sub>2</sub>S inverted to the  $\gamma$ -form.

*Halloysite clay.*—Sinters fired at 1360°C. for four hours were composed almost entirely of new phases whereas those fired at this temperature for one hour contained about 50 percent of material with incomplete new phase development.

EFFECT OF VARIATIONS IN KILN  
ATMOSPHERE

*Kaolinite clays.*—Sinters with a lime-to-alumina ratio of 1.66 and fired in reducing atmospheres differed from similar batches fired under definitely oxidizing conditions by showing more complete reaction at a given firing temperature, more complete inversion of  $C_2S$  to the  $\gamma$ -form, and less pigmentary material. The differences between the sinters fired under the two sets of conditions were, however, very slight, and no new phases were found in the sinters fired in reducing atmospheres.

The foregoing statement does not hold for sinters with high lime contents. For example, sinters with a lime-to-alumina ratio of 2.00 fired under oxidizing conditions showed more complete reaction, more inversion of  $C_2S$  to the  $\gamma$ -form, and less pigment than those fired in a reducing atmosphere.

*Illite and montmorillonite clays.*—Sinters with a lime-to-alumina ratio of 1.66 fired in reducing atmosphere at a given temperature showed better development of new phases, more inversion of  $C_2S$  to the  $\gamma$ -form, and less pigment than those fired under oxidizing conditions. The differences between sinters fired under the two sets of conditions were pronounced although no new phase could be found in the sinters fired in reducing atmosphere.

Like sinters composed of kaolinite clays, the foregoing statements do not hold for sinters of either illite or montmorillonite clays when the lime-to-alumina ratio is high, e.g., 2.00. In such sinters, there was better phase development, more inversion of  $C_2S$  to the  $\gamma$ -form, and less pigment when the firing was done under oxidizing conditions.

*Gibbsite-kaolinite clays.*—A comparison of sinters fired under oxidizing and reducing conditions gives the same results as those noted above for kaolinite clays.

EFFECT OF MISCELLANEOUS VARIATIONS IN  
COMPOSITION

The following data were obtained on sinters prepared with kaolinite clay 877 to which various components were added. The

batches had lime-to-alumina ratios of 1.66 and were held for one hour at 1360°C.

*Titanium.*—No distinct  $TiO_2$  phase could be found in any sinters even when a large percentage of titania had been added to the sinter batch. X-ray diffraction data, however, indicate perovskite ( $CaO \cdot TiO_2$ ) in sinters prepared with added  $TiO_2$ .

*Phosphate.*—Sinters to which 0.05 percent  $P_2O_5$  had been added showed considerable reduction in the amount of  $C_2S$  inverted to the  $\gamma$ -form. As the amount of  $P_2O_5$  in the sinters increased, the amount of  $C_2S$  inverted to the  $\gamma$ -form decreased until in sinters with one percent  $P_2O_5$ , all of the  $C_2S$  remains in the  $\beta$ -form, and therefore no dusting took place.

*Iron.*—In general the only difference that can be detected in the sinters as the content of iron increased is an increase in the amount of the compound  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ . In clays with a low iron content this compound was present in minute ( $2\mu \pm$ ) pigmentary units whereas with larger amounts of iron ( $6\% \pm Fe_2O_3$ ) it occurred in larger masses interstitially between the  $C_2S$  grains.

*Magnesia.*—Sinters prepared from batches with added  $MgCO_3$  frequently contained periclase ( $MgO$ ) in distinct euhedral grains with a diameter of about 60 microns. The calcium silicate in such sinters often had optical characteristics somewhat unusual, such as higher birefringence, suggesting some solid solution phenomenon. It has not been possible, however, to establish any definite correlation between extraction results and the character of such sinters as seen under the microscope.

EFFECT OF VARIATION IN THE CHARACTER  
OF THE LIMESTONE

No differences in character of components could be detected in sinters prepared with either coarse, medium, or fine crystalline limestone. Further, no difference could be detected between such sinters and those prepared with precipitated calcium carbonate. The foregoing statements appear to hold regardless of the clay mineral composition of the clay used in preparing the sinters.

The only conclusion justifiable on the above data is that the size of the calcite units composing a limestone does not determine its suitability for the lime-sinter process.

## X-RAY ANALYSIS

### GENERAL COMMENTS

The method of examination consisted of the registration at room temperature of powder diffraction diagrams of representative whole sinter preparations. Such patterns consist of superpositions of the diffraction patterns of the several individual components, each developed in proportion to the proportion of that component in the sinter.

The ease and accuracy with which a given component can be recognized depends not only on the component itself, but on the accessories which happen to be present in a particular instance. For phases like CaO and MgO, 2 or 3 percent may be clearly evident; for phases like the cubic aluminates, 5 or 10 percent may be necessary for identification, and for phases like the lime silicates, 20 or 30 percent may be somewhat ambiguous. Under such circumstances, little value can be attached to the examination of any one sinter, yet generalizations drawn from a sufficiently varied group of sinters, viewed collectively, may be taken with some confidence.

All of the important phases encountered in the lime sinters are relatively well known from the extensive literature on the constitution of Portland cement.

### PREDOMINANT PHASES

*Calcium orthosilicates.*—Of the three dicalcium silicates, only  $\beta$ -C<sub>2</sub>S and  $\gamma$ -C<sub>2</sub>S are of significance in the lime-sinter process. Of the many studies of the  $\beta$  to  $\gamma$  inversion (and its failure) the most recent one<sup>6</sup> advances the idea that the inversion may be inhibited chemically, on one hand, by foreign ions in the crystal lattice, or, on the other hand, physically, by the isolation from each other of enormous numbers of fine-grained  $\beta$ -C<sub>2</sub>S particles.

The behavior of the lime-sinter preparations seems to be consistent with such a concept. For sinters prepared at 1360°C., those made with kaolinite clays usually inverted fairly rapidly, and to about the same degree. A small amount of  $\beta$ -C<sub>2</sub>S invariably remained uninverted, but it did not keep the sinters from appearing to be completely "dusted." For sinters prepared with clays composed mainly of montmorillonite or illite, however, dusting usually was slow, and occasionally failed altogether. In these sinters the  $\beta$ -C<sub>2</sub>S grains were comparatively large, and in those in which  $\gamma$ -C<sub>2</sub>S was developed it was also clearly larger than in sinters prepared with kaolinite clays. One is led to the conclusion that the more abundant impurities in the latter two types of clays included ions with inhibiting effect.

When the sintering temperature was reduced below about 1300°C., dusting first slowed up, then stopped, even for the kaolinite sinters. In these sinters  $\beta$ -C<sub>2</sub>S was abundantly developed, but the primary particle size was much smaller (by a factor of 100 or more). One can hardly say whether the composition was typical, but the physical condition was clearly conducive to physical inhibition. The material reported by microscopic analysis as showing incomplete development of new phases probably was composed to a considerable extent of such fine particles.

For both the  $\gamma$ -C<sub>2</sub>S, whose crystallization is of the olivene type, and for the  $\beta$ -C<sub>2</sub>S, whose crystallization is not known, minor variations in the cell dimensions were observed which could be attributed to slight variation in chemical composition, but no attempt was made to correlate or interpret such variations. It seemed quite possible that the failure of low temperature  $\beta$ -C<sub>2</sub>S preparations to invert might be due to small departures from the ideal lime-to-silica ratio as well as to physical inhibition.

*Calcium aluminates.*—Three stable aluminates have compositions such that they would be anticipated in materials of the compositions of the various sinter preparations. They are the tri-, penta-, and mono-, referred to respectively as C<sub>2</sub>A, C<sub>5</sub>A<sub>3</sub> and CA. It is commonly claimed that the C<sub>5</sub>A<sub>3</sub>

phase actually runs slightly higher in lime than the formula indicates.

In the region of the compositions employed, there are two eutectic compositions; one involving  $C_2S$ ,  $C_5A_3$ , and  $CA$ , another  $C_2S$ ,  $C_5A_3$ , and  $C_3A$ . Both of these melt below  $1360^\circ C.$ , the normal sintering temperatures used in our studies. In any sinter then, along with the  $C_2S$  and  $C_5A_3$  either some  $C_3A$  or some  $CA$  should also be present. Probable amounts, though, are only from about 10 down to 1 or 2 percent, and detection by the X-ray method is erratic. The  $C_3A$  phase was clearly observed only in one high-lime and high-alumina sinter, and the  $CA$  phase was apparent in only about half of the sinters examined (those sinters which were low in lime).

Comparison of this trend with the trend of extraction data suggests that batch compositions had best be made up with residual lime-to-alumina ratio in the range 1.55 to 1.66 (which includes the  $C_2S$ - $C_5A_3$ - $CA$  eutectic) rather than with a higher ratio (which would include the  $C_2S$ - $C_5A_3$ - $C_3A$  eutectic).

#### LOW TEMPERATURE SYNTHESSES

The course of sinter reactions in the temperature range between the decarbonation of limestone and the normal finishing temperature is best followed by diffraction methods. In order to study these reactions, powder diffraction diagrams were registered for a variety of synthetic mixtures fired at different temperatures. The following conclusions are the result of this work.

*Lime-silica.*—Lime-silica mixtures, in the ratio of  $C_2S$  show extensive reaction at  $1000^\circ C.$  The chief phase developed is  $\beta$ - $C_2S$  which is fine-grained and not subject to inversion. An additional phase is apparently wollastonite, the  $\beta$ - $CS$ , but the amount present does not permit positive identification. Unreacted lime does not exceed 2 or 3 percent. Even as low as  $800^\circ C.$  some reaction is evident, the new phase also apparently being wollastonite.

*Lime-alumina.*—Lime-alumina mixtures, in the ratio of  $C_5A_3$  react slowly over a range from  $1000^\circ$  or  $1100^\circ$  on to  $1300^\circ C.$

or possibly higher. At  $1100^\circ$  it has been possible to observe diffraction effects from  $C_3A$ ,  $C_5A_3$ , and  $CA$  in a single sinter. Continued temperature rise increases the amount of  $C_5A_3$  at the expense of the other aluminates.

The source of alumina is a highly significant factor. Natural aluminous clays resist attack by lime more than does chemically prepared hydrated alumina. Diasporite, for example, dehydrates to corundum at about  $500^\circ C.$ , and some unattacked corundum is still evident in lime sinters fired to  $1200^\circ C.$  Other aluminous clays dehydrate first to an "active"  $\gamma$ -oxide which either may or may not invert to corundum before it can be attacked by free lime. Chemically prepared alumina and hydrated alumina remain active to  $1200^\circ C.$  or higher.

*Lime-kaolinite.*—In the critical temperature range from about  $900^\circ$  to  $950^\circ C.$ , dehydrated kaolinite is not a simple mixture of silica and alumina, but possesses a certain degree of association. This material has been called "metakaolin." Prepared lime-kaolinite mixtures in sinter proportions were fired to a series of intermediate temperatures. At  $1000^\circ C.$  gehlenite is an abundantly developed phase and unreacted free lime is prominent. Little  $\beta$ - $C_2S$  has yet been developed, and the presence of any aluminate is doubtful. From  $1000^\circ$  to  $1300^\circ$  or  $1350^\circ C.$ , free lime and gehlenite gradually disappear and the  $\beta$ - $C_2S$ ,  $C_3A$  and  $C_5A_3$  develop in the order named. The  $\beta$ - $C_2S$  does not become subject to inversion until the firing temperature exceeds  $1300^\circ C.$ , and apparently not until the aluminate phases have adjusted their proportions to the sinter composition. It is suggested that the composition of  $\beta$ - $C_2S$  may also be undergoing some readjustment in this temperature interval.

#### SINTERING PROCESS

The conditions for the preparation of the standard lime sinters, and of the deliberately under-burned sinters described above, differ from the conditions under which thermal curves are registered in that more time is available for progress of the slower reactions. It is apparent in a qualitative way on the differential thermal curves (see page

42) themselves where the thermal effects on reactions involving only one mineral are generally much more prominent than are those involving two solids.

*High alumina and kaolinite clays.*—The endothermic effects up to about 950°C. are all known effects ascribable to individual components.

The intensity of the exothermic effect near 950°C. seems clearly to be correlated with the abundance of kaolinite minerals in the clay, and in turn with the abundance of gehlenite present in sinters finished off at only slightly higher temperatures. It seems not unlikely that the formation of gehlenite from lime and "metakaolin" could be a sufficiently fast process to become apparent in the thermal curves. The even more prominent exothermic effect in the thermal curve of pure kaolinite<sup>7</sup> at this temperature is considered by the authors to represent the collapse of "metakaolin" to mullite. Comparisons of the respective compositions also suggest that comparable heat effects would result from the transition from metakaolin to mullite, or to gehlenite, respectively. It is not possible to say whether this same exothermic effect may also include the formation of some wollastonite.

The further attack of free lime on the gehlenite, or any extraneous material, is a slow, gradual process for which no effects are observable in the curves.

Endothermic effects near the finishing temperature probably represent the melting of some of the material.

*Illite and montmorillonite.*—Curves for the clays composed of these minerals differ from those composed of kaolinite in the lesser significance of the exothermic effect around 950°, and in the presence of prominent effects in the neighborhood of 1200°.

Examination of the sinters reveals that the  $\beta$ -C<sub>2</sub>S developed in them is remarkably coarse-grained. It is suggested that the small alkali (and other impurity) contents of these materials exercise enough mineralizing influence to render the formation of  $\beta$ -C<sub>2</sub>S (and possibly the aluminates) evident in these curves.

## DIFFERENTIAL THERMAL ANALYSES

Differential thermal analysis consists of heating a sample at a constant rate of increase of temperature and recording the temperature at which thermal reactions take place and their intensity. The minerals in a clay may be identified usually from a differential thermal curve,<sup>7</sup> and the development of phases that form when a clay-lime mixture is heated may be studied by the differential thermal curve of such a mixture.

In figure 8 differential thermal curves are given for batches of various types of clay with lime equal to a lime-to-silica ratio of 2.0 and lime-to-alumina ratio of 1.66. The temperature in the analyses was carried to 1400°C. with a rate of increase of about 10°C. per minute. The downward deflections of the curves indicate endothermic reactions, and upward deflections indicate exothermic reactions. A vertical scale for determining the temperature difference indicated by the deflections of the curve is given in figure 9.

*Diaspore clay 872, sinter mixture CS35.*—The endothermic reaction between about 500°C. and 600°C. corresponds to the loss of lattice water (OH) from the diaspore. The endothermic reaction between about 800°C. and 970°C. is due to the loss of CO<sub>2</sub> from the lime carbonate.

Except for a very slight endothermic reaction at about 1325°C., which might be partial fusion, the curve between 970°C. and 1400°C. shows no thermal effect. The reaction at 1325°C. is of such low intensity that it is unlikely that it corresponds to a major reaction of components. Further, if the formation of new phases was accompanied by a distinct thermal reaction, it would be expected to be exothermic rather than endothermic. X-ray and other data show the presence of new phases in material heated to no more than 1360°C., and therefore since the thermal curves do not show distinct reactions, it must be concluded that the new phases form from the lime and dehydrated diaspore without a thermal effect showing on the thermal curves. It would

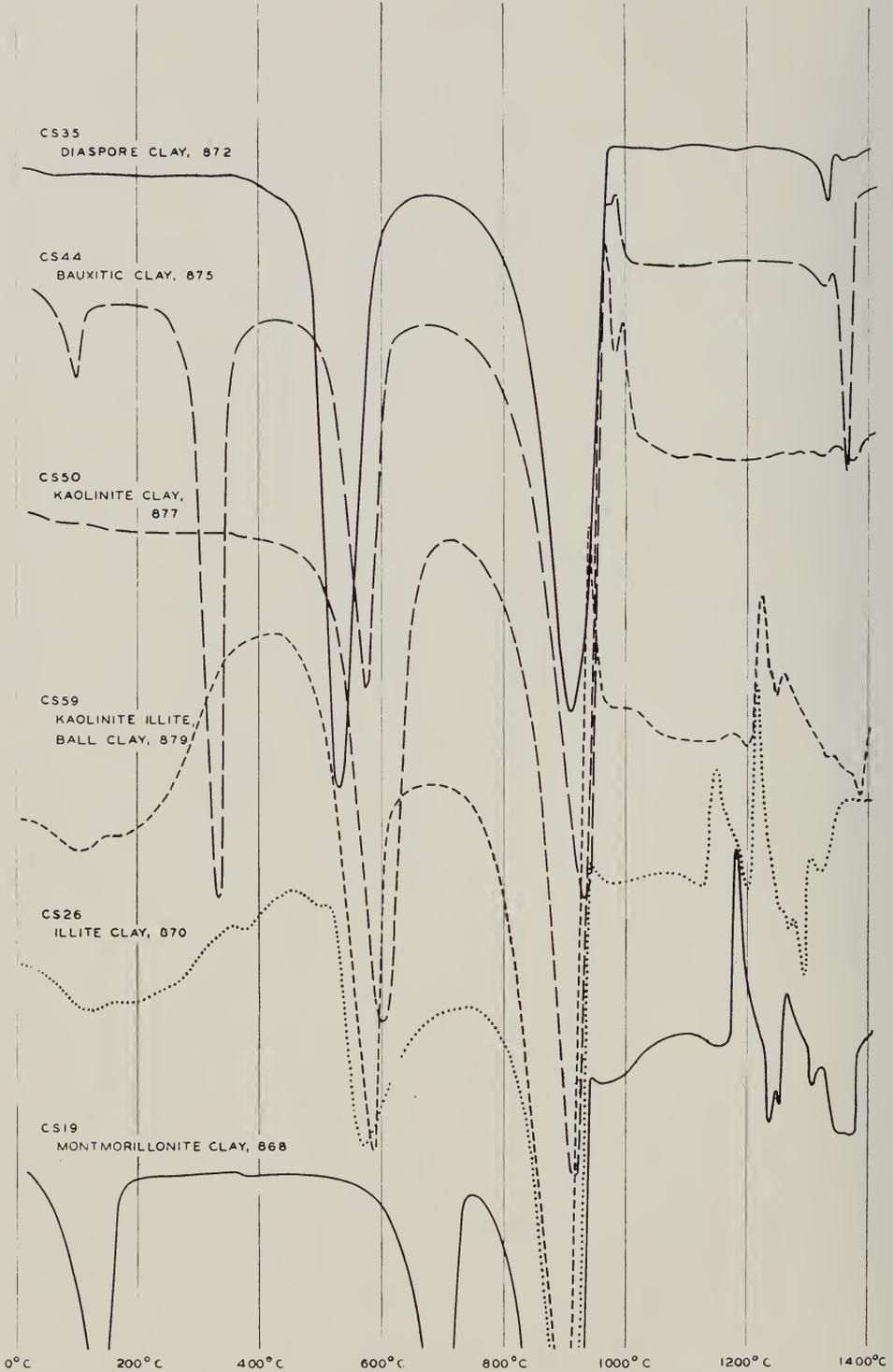


FIG. 8.—Differential thermal analyses of lime-clay sinters. See also fig. 9.

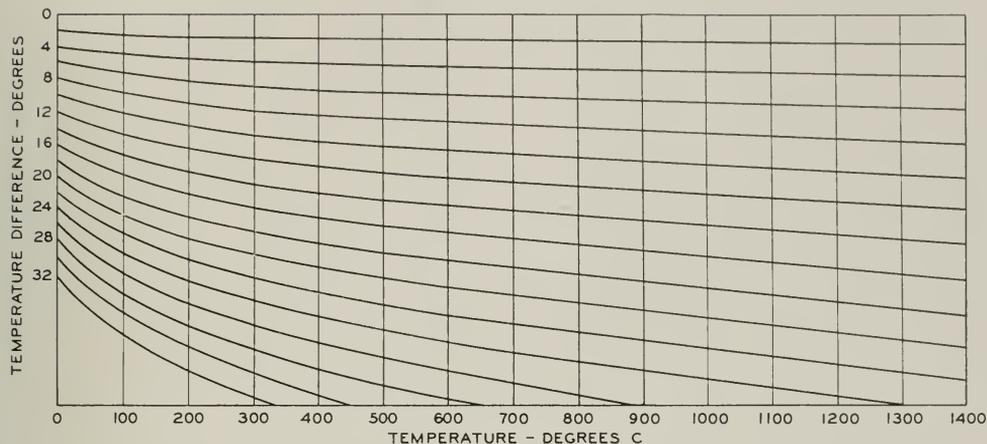


FIG. 9.—Scale for determining the temperature differences recorded by peaks of the differential thermal curves (figs. 8 and 23).

seem that the velocity of such a reaction must be low.

*Kaolinite clay 877, sinter mixture CS50.*—The endothermic reaction with a peak at 600°C. is due to the loss of lattice water (OH) from kaolinite. The endothermic reaction between about 800°C. and 970°C. corresponds to the loss of CO<sub>2</sub> from the lime carbonate.

The reaction due to loss of CO<sub>2</sub> is followed immediately by an exothermic effect indicating that in this clay there is a reaction between components as soon as CaO is formed. X-ray data indicate that this reaction is the formation of gehlenite. Again in this material there is no thermal effect shown by the curves corresponding to the formation of C<sub>5</sub>A<sub>3</sub> and C<sub>2</sub>S and it follows that these new phases are probably formed gradually and slowly.

*Gibbsite-kaolinite clay 875, sinter mixture CS44.*—The initial endothermic peak is due to loss of adsorbed water and suggests that halloysite as well as kaolinite is present in this clay. The endothermic peaks at about 340° and 590°C. are the result of loss of lattice (OH) water from the gibbsite and kaolinite (and halloysite), respectively.

The endothermic reaction between 800°C. and 970°C., due to loss of CO<sub>2</sub> from the lime carbonate, is followed immediately by an exothermic effect which is inter-

preted as resulting from a reaction between the dehydrated kaolinite component and the CaO leading to the formation of gehlenite. The intensity of this exothermic reaction fits with the intensity of the kaolinite dehydration reaction. If this exothermic effect represented a reaction between the CaO and both the dehydrated kaolinite and gibbsite, it would be expected to have greater intensity. Sinters made with this type of clay show the development of C<sub>2</sub>S and C<sub>5</sub>A<sub>3</sub> at least by 1320°C., and since the curves show no thermal effects corresponding to these reactions it would seem that the new phases form gradually and slowly. The endothermic effect at the end of the curve may represent partial melting.

*Illite clay 870, sinter mixture CS26.*—The initial endothermic reaction is due to the loss of adsorbed water, and the endothermic peak at about 575°C. corresponds to the loss of lattice (OH) water from the illite.

The endothermic reaction corresponding to loss of CO<sub>2</sub> is not followed by a distinct exothermic reaction suggesting that dehydrated illite, unlike dehydrated kaolinite, does not react with lime as soon as the CO<sub>2</sub> is driven off. The thermal reactions between 1150°C. and 1225°C. are probably the result of the formation of β-C<sub>2</sub>S and C<sub>5</sub>A<sub>3</sub>.

It would seem that the kind of reaction and temperature of the reaction is different

for the CaO and dehydrated kaolinite, dehydrated illite, dehydrated gibbsite, and diaspore.

*Kaolinite-illite (ball) clay, sinter mixture CS59.*—The initial endothermic peak corresponds to the loss of adsorbed water by the illite, the exothermic reaction between 200°C. and 500°C. is the result of burning off of organic material, and the endothermic peak at about 600°C. is due to the loss of lattice water (OH) from the kaolinite and illite.

The endothermic reaction due to the loss of CO<sub>2</sub> is followed immediately by a small exothermic effect which is interpreted as the result of a reaction between the dehydrated kaolinite portion of the clay and lime to form gehlenite. The exothermic reaction just above 1200°C. is interpreted as the result of a reaction between the dehydrated illite and the lime. This clay composed of two clay minerals, kaolinite and illite, affords an excellent illustration of the different temperatures required for the reaction between the various clay minerals and lime.

*Montmorillonite clay 868, sinter mixture.*—The endothermic peaks at about 150°C. and 700°C. are due to loss of adsorbed water and lattice water (OH), respectively, from the montmorillonite.

Like the illite clay, the reaction due to loss of CO<sub>2</sub> is not followed immediately by an exothermic reaction. Rather there are exothermic reactions at about 1200°C., suggesting that this temperature is required for the reaction of components and the development of new phases.

Montmorillonite is like illite and unlike either kaolinite, gibbsite, or diaspore in the temperatures at which dehydrated components react with the lime to form new phases. The higher temperature to bring about the reaction is probably due to the higher temperature required for the complete destruction of the montmorillonite and illite lattice as compared to the kaolinite lattice. This will be discussed in more detail for the lime-soda-sinters where a similar correlation of reaction temperature and clay mineral type prevails.

## SUMMARY AND CONCLUSIONS

Kaolinite clays and gibbsite-kaolinite (bauxitic) clays gave higher percentage yields of alumina than clays composed of other clay minerals. When such clays were composed of poorly crystallized kaolinite, the yield of alumina was reduced slightly. Halloysite clays gave yields comparable to those for kaolinite clays only if they were heated to unusually high temperatures. The diaspore-clay sinters fused and did not dust so that they are less satisfactory for this process as commonly practiced.

It is probably significant that the more desirable sinters all resulted from those two clay minerals which yield loose active products on roasting, i.e., metakaolin from kaolinite and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from gibbsite.

Within the range of variations in the CaO/Al<sub>2</sub>O<sub>3</sub> ratios from 1.5 to 1.8, only the illite clays, perhaps because of their high iron content, showed considerable variation in the yield of alumina. Illite clays frequently gave considerably higher yields with increased amounts of CaO. In the case of pure kaolinite clays, however, the lime in the mixture can be reduced considerably below the quantity required to give the C<sub>5</sub>A<sub>3</sub> composition without seriously affecting extractability.

Kaolinite, illite, and montmorillonite clays all showed optimum yields when sintering temperatures were around 1360° to 1380°C. Sinters made with illite and montmorillonite clays were more sensitive to overburning than others. At 1360°C. sinters made with diaspore and gibbsite-kaolinite clays fused whereas those made with halloysite clays required sintering temperatures of 1400°C. and higher for moderately good yields.

The yield of alumina from kaolinite and montmorillonite clays was not affected by furnace atmosphere. The effect of variations in the furnace atmosphere on illite clays was erratic except that high iron illite clays gave improved yields when sintered under reducing conditions.

Sinters prepared with illite and montmorillonite clays tended to dust less com-

pletely and less rapidly than sinters made with other types of clay.

The values for  $(100 \times \text{SiO}_2) / (\text{Al}_2\text{O}_3 + \text{SiO}_2)$  were greater for illite and montmorillonite clays than for clays of other types, primarily because of low soluble alumina rather than high soluble silica. Only in the case of kaolinite clays was the silica content decreased by increasing the sintering temperature. Varying the  $\text{CaO} / \text{Al}_2\text{O}_3$  ratio caused small variations in the silica in the extracts from kaolinite, illite, and montmorillonite clay sinters.

In kaolinite-clay sinters fired at a given temperature the yield of alumina decreased as the  $\text{MgO}$  increased up to about 14 percent of the alumina. With further increases in  $\text{MgO}$  up to about 28 percent, the yield of alumina increased. Larger amounts of  $\text{MgO}$  caused no change in alumina yield. The adverse effect of  $\text{MgO}$  on extractability was greater in sinters fired at  $1400^\circ\text{C}$ . than at  $1360^\circ\text{C}$ .

No change in the amount of extractable alumina was encountered when sulphate was added in amounts up to one percent sulphur as  $\text{SO}_3$ .

Phosphate even in small quantities inhibited dusting and sharply reduced the yield of alumina. Iron in the form of  $\text{Fe}_2\text{O}_3$  did not reduce yields of alumina much unless it exceeded one or two percent. In larger amounts iron caused considerable reduction in alumina yield.

Differences in limestone, insofar as they affect the efficiency of the lime-clay-sinter process, are due to factors other than the grain size of the calcite units of which they are composed.

The principal phases developed in the sinters were  $\text{C}_2\text{S}$  ( $2\text{CaO} \cdot \text{SiO}_2$ ) in euhedral grains and  $\text{C}_3\text{A}_3$  ( $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ ) as interstitial material. The  $\text{C}_2\text{S}$  was usually in the  $\gamma$ -form and attained a maximum size of about 10 microns in kaolinite-clay sinters; 60 microns in illite- or montmorillonite-clay sinters.

The compound  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  was present in sinters made with clays containing appreciable iron. The amount of ferrite increased as the lime content increased and was greater in sinters fired under oxidizing

conditions than under reducing conditions. The compounds  $\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  were identified in some sinters in which the lime-to-alumina ratio varied below and above 1.66.

Kaolinite-clay sinters fired at  $1320^\circ\text{C}$ . contained a considerable amount ( $40\% \pm$ ) of material that suggested poor development of new phases. At  $1360^\circ\text{C}$ . the new phases were completely developed, but on increasing the sintering temperature to  $1400^\circ\text{C}$ . the units of  $\text{C}_2\text{S}$  became larger and more completely inverted to the  $\gamma$ -form. New phases were completely developed in illite- and montmorillonite-clay sinters fired to  $1320^\circ\text{C}$ . Higher sintering temperatures served only to increase the size of the  $\text{C}_2\text{S}$  units. New phases were completely developed also in diaspore clay sinters fired at  $1320^\circ\text{C}$ . Gibbsite-kaolinite-clay sinters showed about the same relation to sintering temperature as kaolinite-clays except that there was slightly better phase development at the lower temperature. In the case of halloysite-clay sinters, extensive new phase development was not attained until about  $1450^\circ\text{C}$ . The amount of material with poor phase development in sinters made with kaolinite and halloysite clays was reduced by increasing the time the sinter was held at the top temperature.

X-ray diffraction analysis indicates that the material suggesting poor development of new phases was largely  $\beta$ - $\text{C}_2\text{S}$  in extremely fine units in which minor variations in cell dimensions have been observed that could retard inversion to the  $\gamma$ -form.

X-ray and differential thermal analyses suggest that in diaspore clay sinters the reaction of components to form new phases began as soon as the  $\text{CO}_2$  was driven off and continued slowly without pronounced thermal effects. In the case of kaolinite clays the loss of  $\text{CO}_2$  was followed immediately by the formation of gehlenite which was accompanied by a sharp endothermic reaction at about  $950^\circ\text{C}$ . In such mixtures (kaolinite clay) fired  $1000^\circ\text{C}$ ., gehlenite and free lime were prominent phases. As the temperature was carried from  $1000^\circ$  to  $1300^\circ\text{C}$ ., free lime and gehlenite disappeared gradually and the  $\beta$ - $\text{C}_2\text{S}$ ,  $\text{C}_3\text{A}$  and  $\text{C}_5\text{A}_3$

developed in the order named, the latter at the expense of  $C_3A$ .

X-ray and differential thermal analyses for mixtures of illite and montmorillonite clays did not indicate the formation of gehlenite. Apparently there was little reaction of components until about  $1200^{\circ}C$ . when the  $\beta-C_2S$  and possibly the aluminates

developed sharply with a pronounced thermal effect. The higher temperature required for the reaction of illite and montmorillonite with lime than for kaolinite and lime was probably the result of the higher temperatures required for the destruction of the lattice structure of the former clay minerals.

## LIME-SODA-SINTER PROCESS

From the chemical viewpoint the lime-soda-sinter process is not fundamentally different from the lime-sinter process. The ground siliceous alumina-bearing ore is mixed with calcium carbonate and sodium carbonate in the proportions to give a mixture corresponding approximately in percentage composition (ignoring volatile constituents) to a mixture of dicalcium silicate and sodium aluminate,  $\text{NaAlO}_2$ . The mixture is then heated to such temperature and for such a period of time as may be necessary to render a maximum proportion of alumina and soda and a minimum proportion of other materials present soluble in dilute alkali-carbonate solution. The temperature necessary is not so high and not so critical as for the lime-sinter process. As in the lime-sinter process the primary function of the lime is to tie up the silica in a form not soluble in the leach liquor. The transformation of dicalcium silicate when or if it occurs does not result in dusting of the sinter. The sintered mass is usually considerably less dense than that produced when the lime-sinter method is used. It is rather friable, porous, and easily ground when not overburned.

The clay samples used in these experiments, after mixing with  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$  and heating, gave sintered materials in which the compositions in percent for the important oxides were about as follows in most cases.

|   | Kaolinite clays<br>(percent) | Illite and<br>Montmorillonite clays<br>(percent) |
|---|------------------------------|--|
| $\text{SiO}_2$ .....                          | 23                           | 26   |
| $\text{Al}_2\text{O}_3$ .....                 | 20                           | 9  |
| $\text{CaO}$ .....                            | 44                           | 53   |
| $\text{Na}_2\text{O} + \text{K}_2\text{O}$ .. | 12                           | 6  |

Sinters made from the very high alumina clays and bauxites, of course varied considerably from the above values. Halloysite clay sinters were similar to kaolinite clay sinters in composition.

Equilibrium data on the four-component system  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{Na}_2\text{O}$ - $\text{CaO}$  are not available on which estimates of fusion points

can be based, but experiment has shown that most of these sinters are only partially fused at  $1300^\circ\text{C}$ . Hence, it is to be predicted that an equilibrium state will probably not be reached at lower temperatures unless the mixtures are held at those temperatures for considerable periods of time. The presence of iron, magnesia, phosphorus, and titania, even in minor amounts, cannot safely be presumed to be without influence on the final state reached under a given set of operating conditions. The nature of the various clay mineral types, which react differently when heated, might be expected to have an important effect on the final state reached when such mixtures are heated unless the heating is carried far enough to produce complete or nearly complete fusion of the sinter mix. The data presented were collected from experiments designed to study the influence of some of these factors in the lime-soda-sinter process.

## EXPERIMENTAL METHODS

## PREPARATION OF SINTER SAMPLES

Clay samples were ground to pass 80 mesh, calcined at  $800^\circ\text{C}$ . (Sample No. 872 diaspore was not calcined, see page 14), mixed carefully with the appropriate quantities of precipitated  $\text{CaCO}_3$  and C. P. grade anhydrous  $\text{Na}_2\text{CO}_3$ . The batches were then pressed into cylindrical briquets  $1\frac{3}{8}$  inches in diameter under a pressure of 5000 pounds per square inch.

Except in work planned to study the effect of varying amounts of lime or soda, batches were made up with sufficient  $\text{CaCO}_3$  to furnish two moles of  $\text{CaO}$  for each mole of  $\text{SiO}_2$  and enough  $\text{Na}_2\text{CO}_3$  to supply one mole of  $\text{Na}_2\text{O}$  for each mole of  $\text{Al}_2\text{O}_3$ . In calculating the amount of  $\text{Na}_2\text{CO}_3$  to be added, account was taken of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  occurring naturally in the clay.  $\text{K}_2\text{O}$  was considered equivalent to  $\text{Na}_2\text{O}$  mole for mole.

The briquets were placed in a cold electrically-heated muffle furnace, heated in a manner indicated by the recorder trace

(fig. 15) except as noted otherwise in special instances. The briquets were placed in tightly closed bottles as soon as they became cool enough to handle.

A few sinters were made with the briquets resting on a graphite block which in turn rested on the floor of the muffle. The color of such briquets indicated that the furnace atmosphere was reducing under these conditions. Since oxidizing conditions are normal in commercial kilns, measures were taken to insure oxidizing conditions in the test furnace except as otherwise noted for studies on the effect of furnace atmosphere. The briquets thereafter were supported in small clay dishes with a thin briquet of composition identical with that of the test briquet interposed between the dish and the test briquet. After sintering, the thin briquet was discarded. No trouble was encountered until the temperature 1300°C. was reached when the corrosive action of the briquet on the clay dishes began to be serious with briquets made from most of the clays. Briquets from clays containing considerable iron showed signs of incipient fusion at 1300°C. Briquets from fairly clean kaolins could probably be heated to temperatures somewhat higher than 1300°C. without much distortion if supported on graphite or otherwise protected from the slagging action of the clay dish. As a rule the sinters shrank during the heating process, although some prepared at the lower temperatures swelled noticeably.

#### CHEMICAL ANALYSIS OF SINTERS

The sintered material was analyzed for silica and  $R_2O_3$  by standard methods. The values for alumina were obtained by correcting the  $R_2O_3$  values for  $Fe_2O_3$  and  $TiO_2$  as calculated from the batch.

#### EXTRACTION OF ALUMINA FROM SINTERED MATERIAL AND ANALYSIS OF EXTRACTS

After some preliminary experimenting the method of extraction described below was adopted as the standard procedure for this series of tests. The sintered briquet was ground to pass 65 mesh. A 10-gram sample

was weighed out, and the quantity of  $Al_2O_3$  present in the sample was calculated from the batch composition. A quantity of  $Na_2CO_3$  (in the form of a standard solution) was taken, sufficient so that the total  $Na_2O$  available including that in the sinter amounted to 1.8 moles  $Na_2O$  per mole of  $Al_2O_3$  in the 10-gram sinter sample. This  $Na_2CO_3$  solution was diluted to 100 cc., heated to 65°C., and maintained at this temperature while the ground sinter was introduced in such manner that no lumps were formed. The suspension was stirred with a motor stirrer for 15 minutes, at a rate which would prevent sedimentation, and filtered immediately with suction. The solution was made up to 250cc. and analyzed gravimetrically for  $Al_2O_3$  and colorimetrically for  $SiO_2$ .

### EXPERIMENTAL RESULTS

#### EFFECT OF TYPE OF CLAY MINERALS OPTIMUM YIELD OF ALUMINA

The factors which may be varied at the will of the operator of a plant producing alumina by the lime-soda sinter process are the lime-clay and soda-clay ratios, the temperature, the duration of the heating period, and to a lesser extent the furnace atmosphere. Proper adjustment of these variables with relation to one another might be expected to result in an optimum yield for a given raw material, assuming good extraction practice. Data are presented in graphic and tabular form in table 12 and figures 11, 12, 13, and 14, which bear on the effect of these operating variables when various types of clays are used in the sinter mix under laboratory conditions. Variables connected with the extraction process were not considered except that care was taken to keep the extraction conditions standardized.

The data indicate that the kaolinite clays and gibbsite-kaolinite (bauxitic) clays may yield more than 90 percent of their alumina when clean, that is, when such clays are relatively free from iron and clay minerals other than kaolinite and gibbsite. Halloysite and montmorillonite clays and anortho-

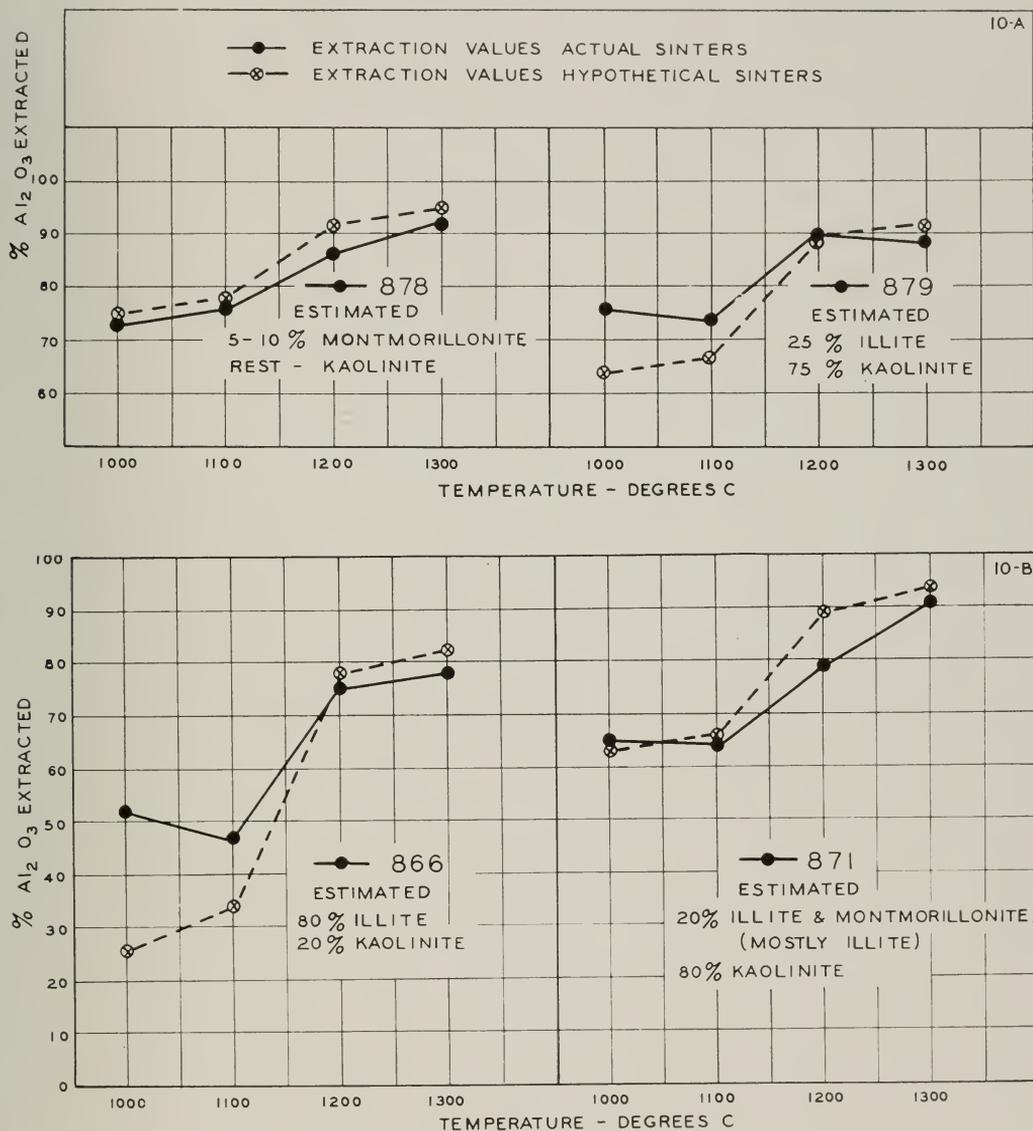


FIG. 10.—Parts A and B

Comparison of actual extraction values for lime-soda sinters prepared from clays containing more than one clay mineral type with hypothetical mixtures of clay: 877 kaolinite, 870 illite, and 868 montmorillonite.

site yielded nearly as great a percentage of their alumina as the kaolins, but it was somewhat more difficult to get top yields. The top yields from illite clays ran 10 or 12 percent below those from the other clays. The single diaspore clay studied did not yield quite as high a percentage of its alumina as most of the kaolins.

Clays which are composed of mixtures of clay minerals behaved about as would be predicted from a consideration of the behavior of the nearly pure types. The graphs in figure 10 are comparisons of actual yields from clays which contain considerable amounts of more than one type of clay mineral with hypothetical mixtures of pure types. For example, clay 879 was estimated to contain 25 percent illite and 75 percent kaolinite. The yield from clay 877 (pure kaolinite) at 1200°C. was 94 percent; that from clay 870 (nearly pure) illite was 76 percent. Seventy-five and twenty-five percent of these values were 70.5 and 19

respectively. The sum of these is 89.5 which is taken as the yield of a hypothetical mixture containing three parts by weight of clay 877 and one part by weight of clay 870.

Hypothetical yields from mixtures of 877 (kaolinite) with 870 (nearly pure illite) and with 868 (nearly pure montmorillonite) are plotted on the same diagrams (fig. 10) with actual yields from clays 866, 871, 878, and 879. The agreement is considered good, taking into account the difficulty of making accurate estimates of the relative amounts of the clay minerals in a natural mixture and that there are factors other than the clay mineral types which are difficult or impossible to evaluate.

#### SINTERING TEMPERATURE

Fourteen representative types of clay materials and one anorthosite comprising samples 865, 866, 867, 868, 869, 870, 871, 872, 875, 877, 878, 879, 881, 883, and 884

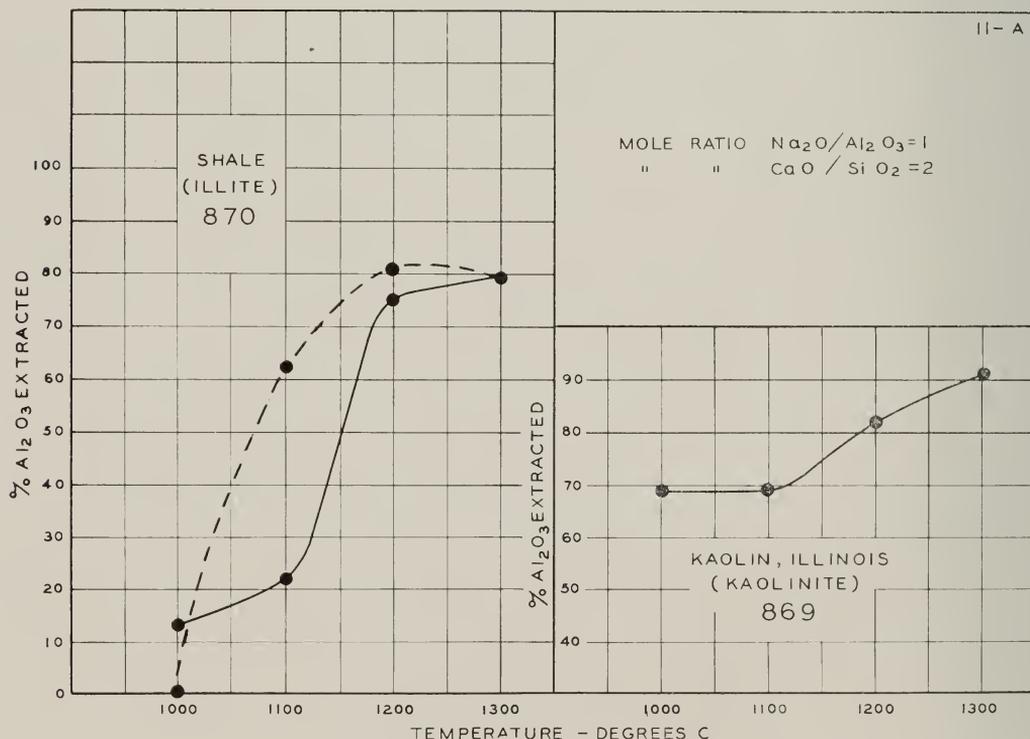


FIG. 11.—Part A

Percent  $\text{Al}_2\text{O}_3$  extracted versus temperature at which sinter was held for ten minutes. See pp. 52.

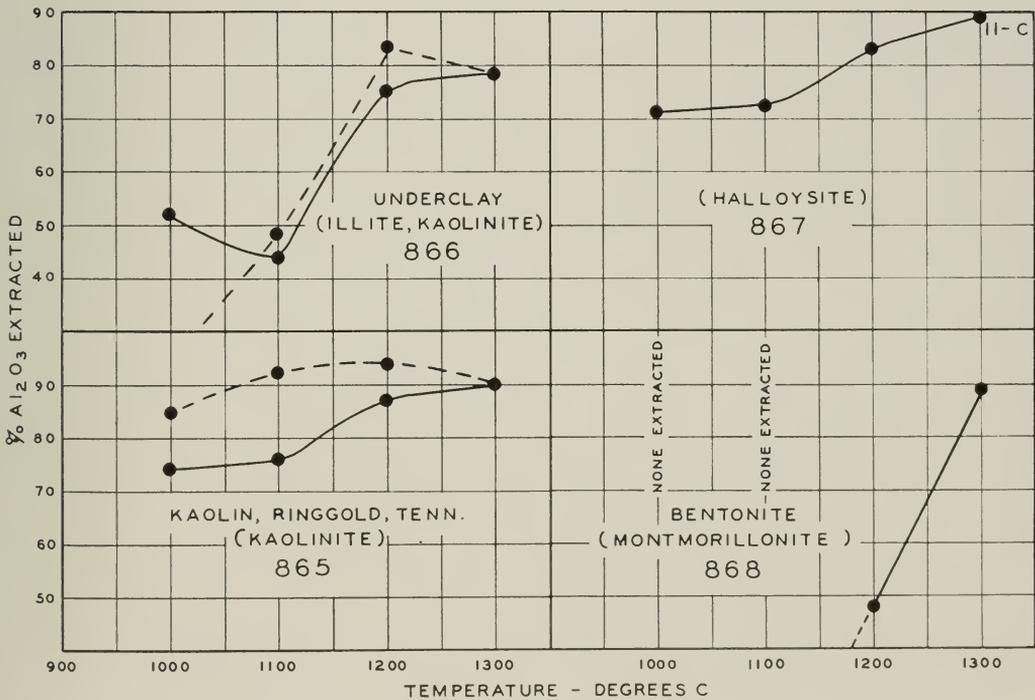
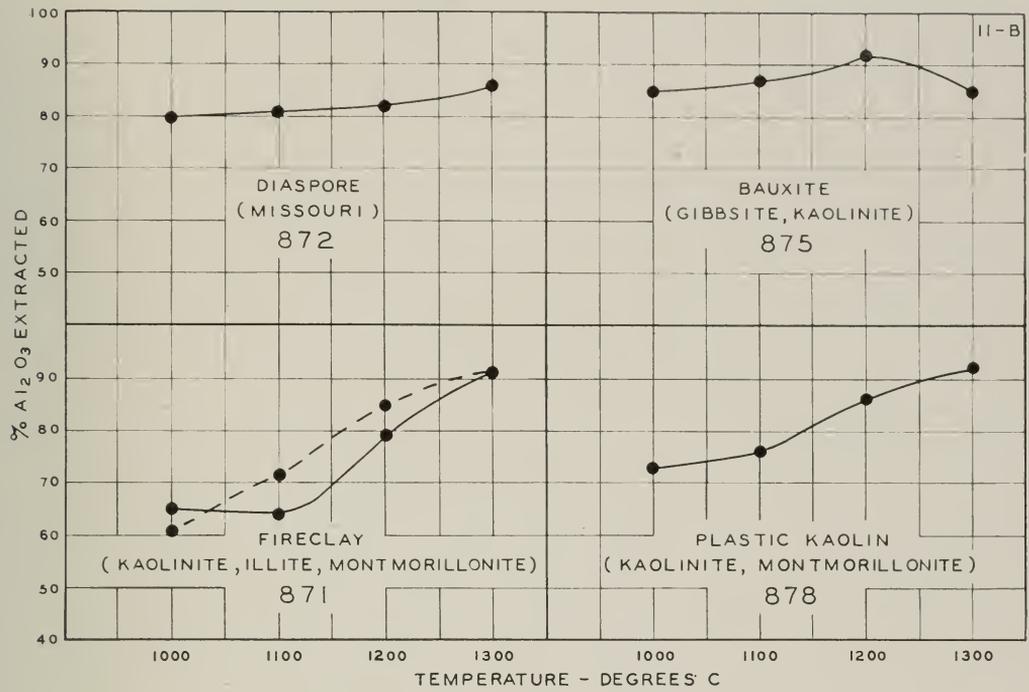
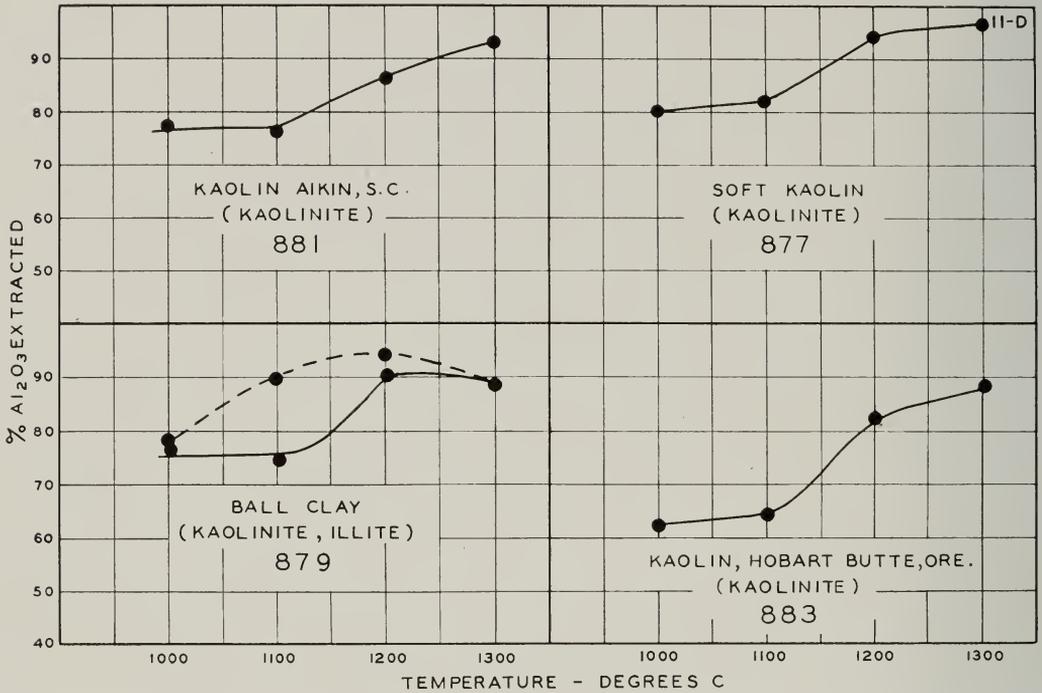


FIG. 11.—Parts B and C

Percent  $Al_2O_3$  extracted versus temperature at which sinter was held for ten minutes.

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were mixed with  $\text{CaCO}_3$  and  $\text{Na}_2\text{CO}_3$ . The mole ratio of soda to alumina was one and that of lime to silica was two. Briquets made from each were heated up to top temperatures ranging from  $1000^\circ\text{C}$ . to  $1300^\circ\text{C}$ . as indicated in table 12, held there for ten minutes, allowed to cool, ground, and extracted. The data are presented in table 12 and in figure 11.

It will be noted that the curves showing the behavior of clays of a given type are quite similar in shape although the yields of soluble alumina vary considerably. For some clays the yields from sintering at  $1000^\circ\text{C}$ . and  $1100^\circ\text{C}$ . are about the same but there is a definite increase in yield when the temperature is raised to  $1200^\circ\text{C}$ . and higher. The reason for this break is partly that, since it required longer to heat to the higher temperature, the effect involves both a time and a temperature factor, which circumstance tends to magnify any increase in extractability due to increased temperature. In some cases where the variation was most extreme a new series of sinters was made for which the time that the sinters were kept above  $1000^\circ\text{C}$ . was held constant

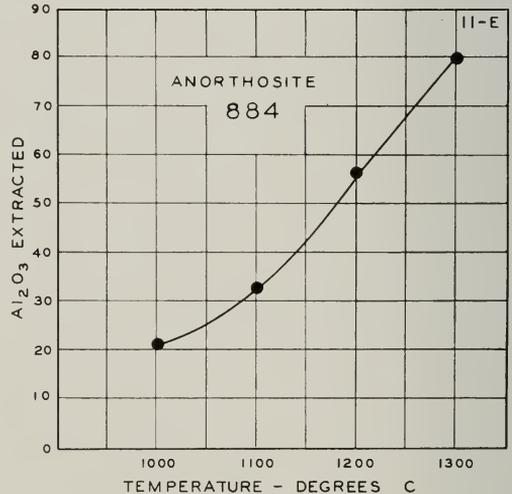


FIG. 11.—Parts D and E  
Percent  $\text{Al}_2\text{O}_3$  extracted versus temperature at which sinter was held for ten minutes.

and equal to three hours, as nearly as this could be done. This was done for clays 865, 866, 870, 871, and 879, and the resulting data appear on figure 11 as dotted line curves.

Kaolinite clays, if quite pure, gave nearly the same percentage yield of alumina for all temperatures in the range  $1100^\circ\text{C}$ . to  $1300^\circ\text{C}$ . when the time was the same. The opti-

imum temperature is probably about 1200° C. Yields ranging upward from 75 percent of total alumina are obtainable from good kaolinite clays even at 1000° C. Imperfectly crystallized kaolinite clays such as 869 and 883 did not yield so well, especially at the lower temperatures.

Sinters prepared from gibbsite-kaolinite clays are less sensitive to temperature variation than those from kaolinite clays. The yields were about the same at 1000° C. as at 1300° C. despite the fact that the heating period was longer at the higher temperature.

Sinters prepared from diasporic clay behave toward variation of temperature much like those from gibbsite-kaolinite clays. The small rise in yield with increasing temperature noted for 872 was probably mostly due to the longer period required to reach the higher temperatures.

No alumina could be extracted from sinters prepared from montmorillonite clay at temperatures up to 1100° C. Even at 1200° C. only half of the alumina was made soluble. The extraction yield went up to 90 percent at 1300° C.

TABLE 12—EFFECT OF SINTERING TEMPERATURE ON PERCENT  $Al_2O_3$  EXTRACTED WITH VARIOUS TYPES OF CLAY.

Time at top temperature—10 minutes

$Na_2O/Al_2O_3 = 1$ ;  $CaO/SiO_2 = 2$ ; see Figure 14

| Clay Sample No. | Sinter No. | Sinter Temp. Degrees C. | Percent $Al_2O_3$ in Sinter | Percent $Al_2O_3$ Extracted | $\frac{100 SiO_2}{Al_2O_3 + SiO_2}$ |
|-----------------|------------|-------------------------|-----------------------------|-----------------------------|-------------------------------------|
|                 |            |                         |                             |                             | in extract                          |
| 865.....        | 51         | 1000                    | 19.7                        | 74                          | 1.2                                 |
|                 | 37         | 1100                    | "                           | 76                          | 2.4                                 |
|                 | 70         | 1200                    | "                           | 87                          | 2.1                                 |
|                 | 82         | 1300                    | "                           | 90                          | 1.8                                 |
| 866.....        | 52         | 1000                    | 9.7                         | 52                          | 0.2                                 |
|                 | 38         | 1100                    | "                           | 44                          | 1.4                                 |
|                 | 71         | 1200                    | "                           | 75                          | 2.7                                 |
|                 | 83         | 1300                    | "                           | 85                          | 1.7                                 |
| 867.....        | 53         | 1000                    | 21.2                        | 71                          | 1.8                                 |
|                 | 39         | 1100                    | "                           | 72                          | 2.0                                 |
|                 | 72         | 1200                    | "                           | 83                          | 1.9                                 |
|                 | 84         | 1300                    | "                           | 89                          | 1.7                                 |
| 868.....        | 54         | 1000                    | 9.2                         | —                           | —                                   |
|                 | 40         | 1100                    | "                           | —                           | —                                   |
|                 | 73         | 1200                    | "                           | 44                          | 1.5                                 |
|                 | 85         | 1300                    | "                           | 89                          | 1.7                                 |
| 869.....        | 55         | 1000                    | 15.0                        | 69                          | 1.3                                 |
|                 | 41         | 1100                    | "                           | 69                          | 2.5                                 |
|                 | 69         | 1200                    | "                           | 82                          | 2.4                                 |
|                 | 86         | 1300                    | "                           | 90                          | 2.2                                 |
| 870.....        | 56         | 1000                    | 9.5                         | 13                          | 2.4                                 |
|                 | 42         | 1100                    | "                           | 22                          | 0.0                                 |
|                 | 75         | 1200                    | "                           | 75                          | 3.8                                 |
|                 | 87         | 1300                    | "                           | 79                          | 1.8                                 |
| 871.....        | 57         | 1000                    | 13.3                        | 65                          | 2.3                                 |
|                 | 43         | 1100                    | "                           | 64                          | 2.5                                 |
|                 | 76         | 1200                    | "                           | 79                          | 2.2                                 |
|                 | 88         | 1300                    | "                           | 91                          | 1.8                                 |
| 872.....        | 58         | 1000                    | 46.1                        | 80                          | 2.6                                 |
|                 | 44         | 1100                    | "                           | 81                          | 2.1                                 |
|                 | 66         | 1200                    | "                           | 82                          | 2.1                                 |
|                 | 89         | 1300                    | "                           | 86                          | 1.6                                 |

TABLE 12—Continued

| Clay Sample No. | Sinter No. | Sinter Temp. Degrees C. | Percent Al <sub>2</sub> O <sub>3</sub> in Sinter | Percent Al <sub>2</sub> O <sub>3</sub> Extracted | 100 SiO <sub>2</sub>  |
|-----------------|------------|-------------------------|--|--|---|
|                 |            |                         |  |  | Al <sub>2</sub> O <sub>3</sub> +SiO <sub>2</sub> in extract |
| 875.....        | 59         | 1000                    | 32.1   | 85   | 2.5   |
|                 | 45         | 1100                    | 32.2   | 87   | 1.8   |
|                 | 77         | 1200                    | 32.2   | 92   | 2.2   |
|                 | 90         | 1300                    | 34.3   | 85   | 2.0   |
| 877.....        | 64         | 1000                    | 19.4   | 80   | 2.9   |
|                 | 50         | 1100                    | 19.6   | 82   | 2.3   |
|                 | 65         | 1200                    | 19.9   | 94   | 1.9   |
|                 | 95         | 1300                    | 20.2   | 96   | 1.8   |
| 878.....        | 60         | 1000                    | 17.7   | 73   | 2.7   |
|                 | 46         | 1100                    | 17.7   | 76   | 2.3   |
|                 | 78         | 1200                    | 17.9   | 86   | 1.9   |
|                 | 91         | 1300                    | 18.0   | 91   | 1.9   |
| 879.....        | 61         | 1000                    | 16.5   | 76   | 2.0   |
|                 | 47         | 1100                    | 16.5   | 74   | 2.1   |
|                 | 79         | 1200                    | 16.7   | 90   | 2.0   |
|                 | 169        | 1300                    | 16.7   | 89   | 1.9   |
| 881.....        | 62         | 1000                    | 18.7   | 77   | 2.3   |
|                 | 48         | 1100                    | 18.6   | 76   | 2.2   |
|                 | 80         | 1200                    | 19.0   | 86   | 2.3   |
|                 | 93         | 1300                    | 19.1   | 93   | 2.0   |
| 883.....        | 63         | 1000                    | 17.0   | 62   | 2.2   |
|                 | 49         | 1100                    | 17.4   | 64   | 2.1   |
|                 | 81         | 1200                    | 17.5   | 82   | 1.8   |
|                 | 94         | 1300                    | 17.7   | 87   | 1.8   |

Sinters prepared from illite clays yielded poorly at temperatures up to 1100°. The yield was much higher at 1200°C. but little was gained by increasing the temperature above 1200°C.

#### EFFECT OF TIME HELD AT TOP SINTERING TEMPERATURE

A series of briquets was prepared in which the mole ratio of soda to alumina was one and that of lime to silica was two. These briquets were then heated to 900°C. at a rate of about 50° per hour. The rate was then increased to approximately 250° per hour and continued until the temperature reached 1100°C. The temperature of 1100°C. was held for 10 minutes with one set of briquets, 60 minutes for another set, and 120 minutes for a third set. The temperature of 1100°C. was selected because the extraction values for short sintering periods at this temperature were low

enough to allow improvement with more extended periods.

The results obtained from this series of tests are presented graphically in figure 12. All samples except the montmorillonite clay showed some improvement in yield of alumina with increased time of heating. Anorthosite showed more improvement than any of the clays. This is probably because of the relatively large size of the anorthosite particles in comparison with the clay mineral particles that make up clays. Although the anorthosite was ground so that 90 percent passed the 200-mesh sieve, individual particles are relatively large. Each 200-mesh particle of anorthosite can be visualized as a single fragment of this mineral. On the other hand, a 200-mesh particle of clay is composed of a large number of smaller single particles aggregated together. Furthermore, the breakup of the clay structure on heating might be expected to result in a porous material which pre-

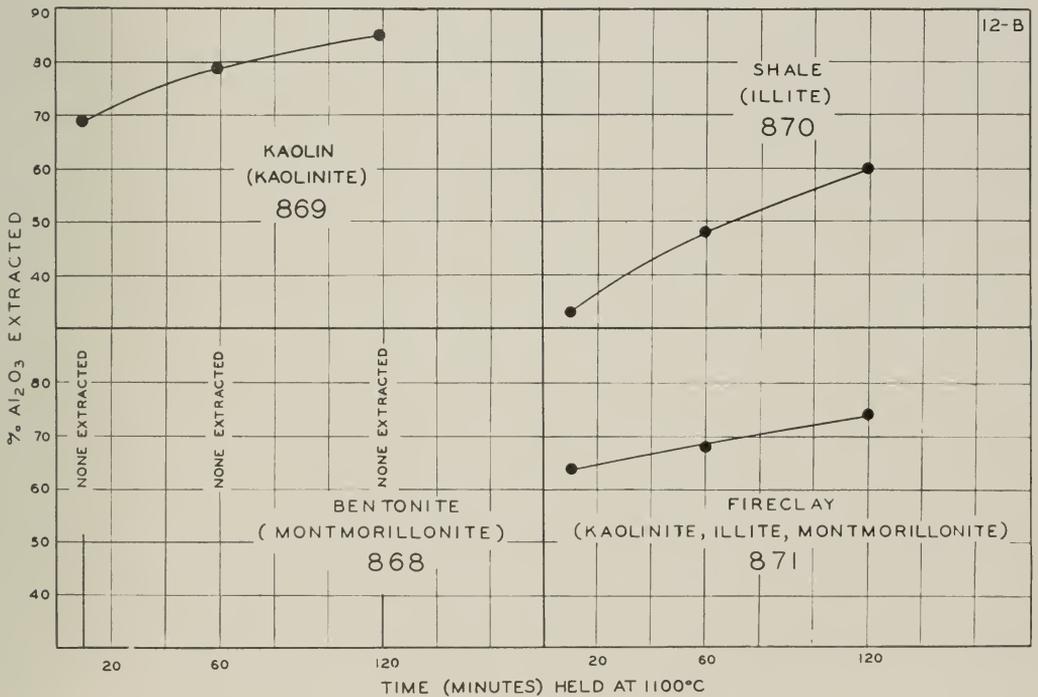
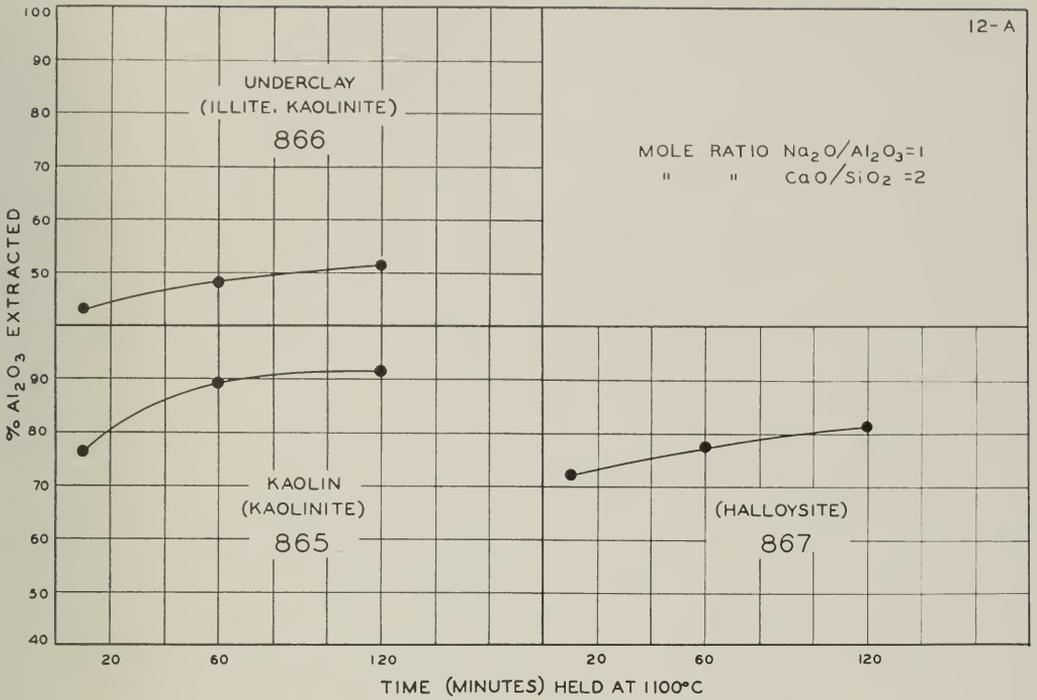


FIG. 12.—Parts A and B  
 Percent  $\text{Al}_2\text{O}_3$  extracted versus time sinter was held at  $1100^\circ\text{C}$ .

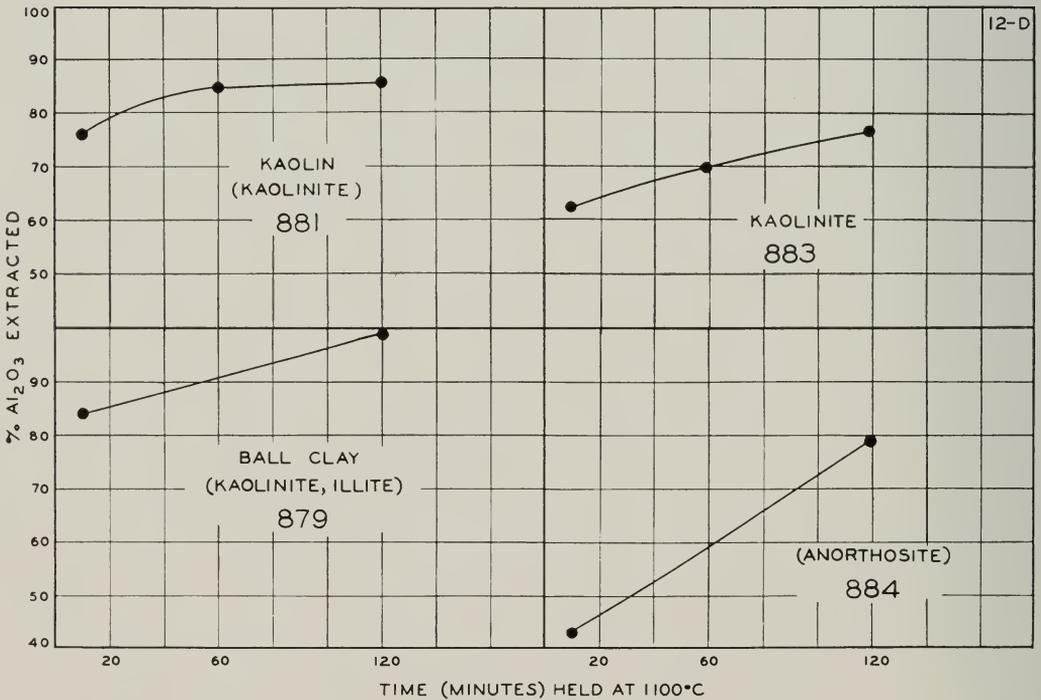
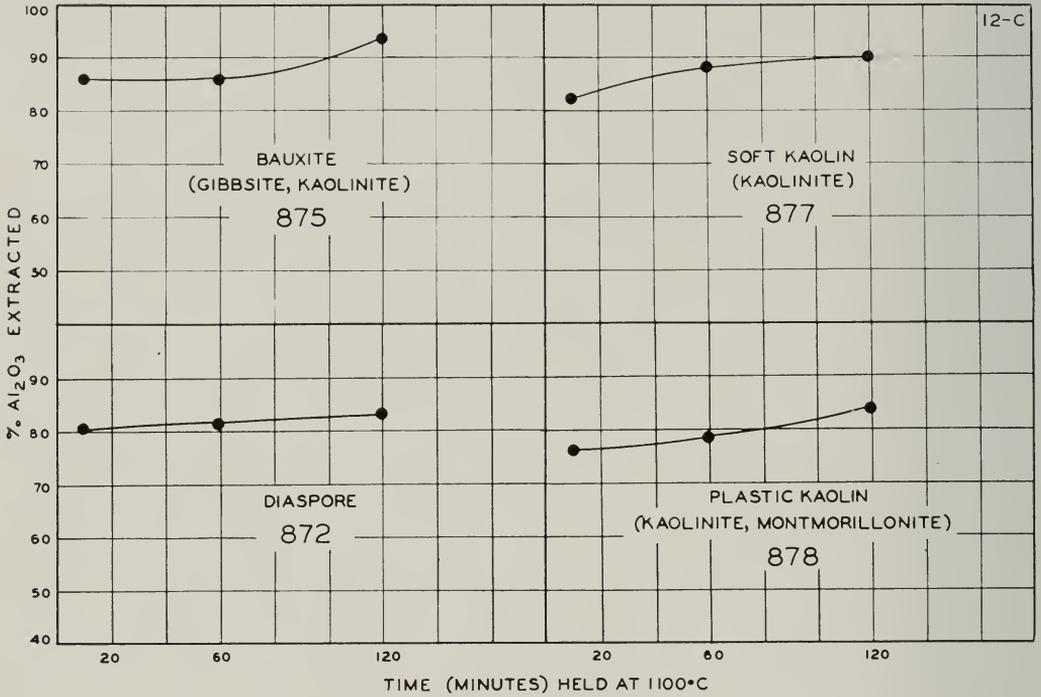


FIG. 12.—Parts C and D  
Percent  $\text{Al}_2\text{O}_3$  extracted versus time sinter was held at  $1100^\circ\text{C}$ .

sumably could absorb molten sodium carbonate so as to allow relatively quick reaction all the way to the center of the particles. The less porous anorthosite unit would be exposed to the action of soda and lime only at the surface of the particle.

Sinters prepared from pure kaolinite clays showed continuous though moderate improvement with increasing time. The yield from those prepared from imperfectly crystallized kaolinite clays (869 and 883) improved more with increasing time than did the others.

Sinters prepared from diasporic clay were less affected by the time of sintering than those prepared from kaolinite clay.

Sinters prepared from gibbsite-kaolinite clay behaved much like those prepared from kaolinite clays toward time variation except that the improvement in alumina yield was somewhat less.

Sinters prepared from illite clay 870 showed great and nearly linear improvement with increased sintering time but those from clay 866 (estimated to contain 80 percent illite) improved only moderately with increased time. Possibly the reason for the difference is related to the fact that the iron content is very high in clay 870.

No alumina could be extracted from sinters prepared from the montmorillonite clay heated to 1100°C. even after sintering for 120 minutes at this temperature.

#### EFFECT OF HEATING RATE

A series of briquets, covering the same samples and made up to the same specifications as those used in the series discussed in the preceding section were heated to 1100°C. on a heating schedule in which the rate of increase averaged about 50°C. per hour over the range from 900° to 1100°C. The part of the heating schedule below 900° was similar to that illustrated in figure 15. The yields of soluble alumina were almost exactly the same in nearly all cases as those shown on figure 12 for the period in which the sinters were held at 1100°C. for 60 minutes. These sinters (figure 12, 60 minutes) were above 1000°C. for about 95 minutes, whereas

the sinters heated at the slower rate were above 1000°C. for about 120 minutes. There was, therefore, no considerable effect on the yield which could be ascribed to the slow rate of heating. The character of the briquets was, however, noticeably different in that they were more friable than similar briquets heated to the same top temperature at a more rapid rate. Some of them had increased in diameter as much as  $\frac{1}{8}$  inch. Others, although showing some shrinkage, did not shrink as much as similar briquets which had been heated more rapidly.

#### EFFECT OF FURNACE ATMOSPHERE

Sinters were made at 1200°C. using the same composition for the sinter mixes as in the tests described in the two preceding sections with the furnace atmosphere rendered strongly reducing by passing a current of natural gas into the furnace. Comparison of the extraction yields from these sinters with those from similar sinters burned under the normal oxidizing conditions at the same temperature disclosed no differences which could certainly be correlated with atmosphere. There were two cases in which considerably better yields were obtained with reducing atmospheres than with oxidizing atmospheres. These were from sinters prepared with the montmorillonite clay and with the anorthosite. However, it is not considered that the small amount of data justify more than a tentative conclusion in these two instances.

#### EFFECT OF SODA-TO-ALUMINA RATIO

A series of sinters was made in which the mole ratio of soda to alumina was 0.8, 1.0, and 1.2. The results obtained from these tests are presented in figure 13. In all cases the effect of increasing the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio was an improvement in the yield of soluble alumina. The degree of improvement, however, varied greatly. The data are erratic in some cases. This frequently happened when some of the sinters were rather completely vitrified. When such a sinter is ground to pass 65-mesh in preparation for extraction it will contain more particles close to 65-mesh size and fewer

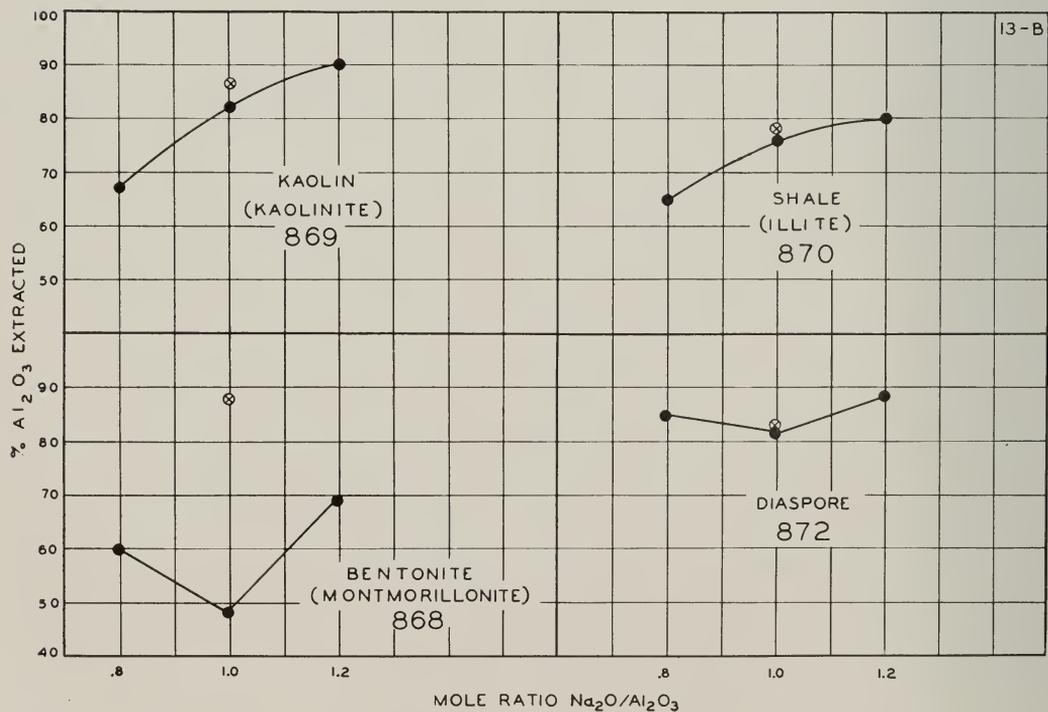
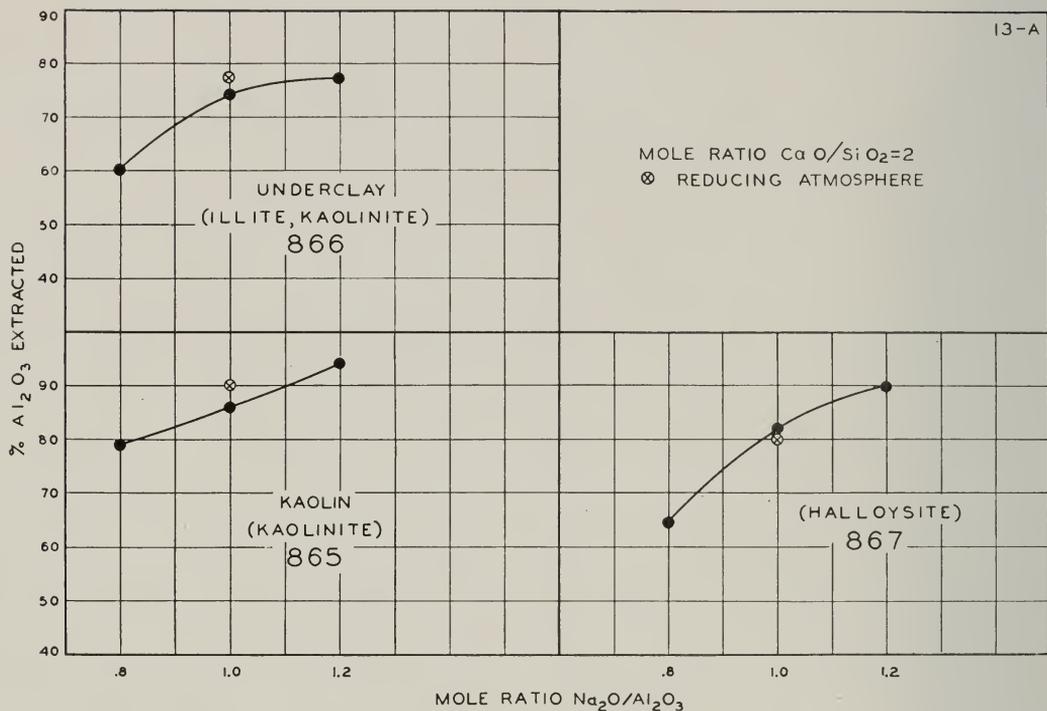


FIG. 13.—Parts A and B  
 Percent  $\text{Al}_2\text{O}_3$  extracted versus mole ratio  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$   
 Sinter temperature  $1200^\circ\text{C}$ .; sinter time 10 minutes at top temperature.

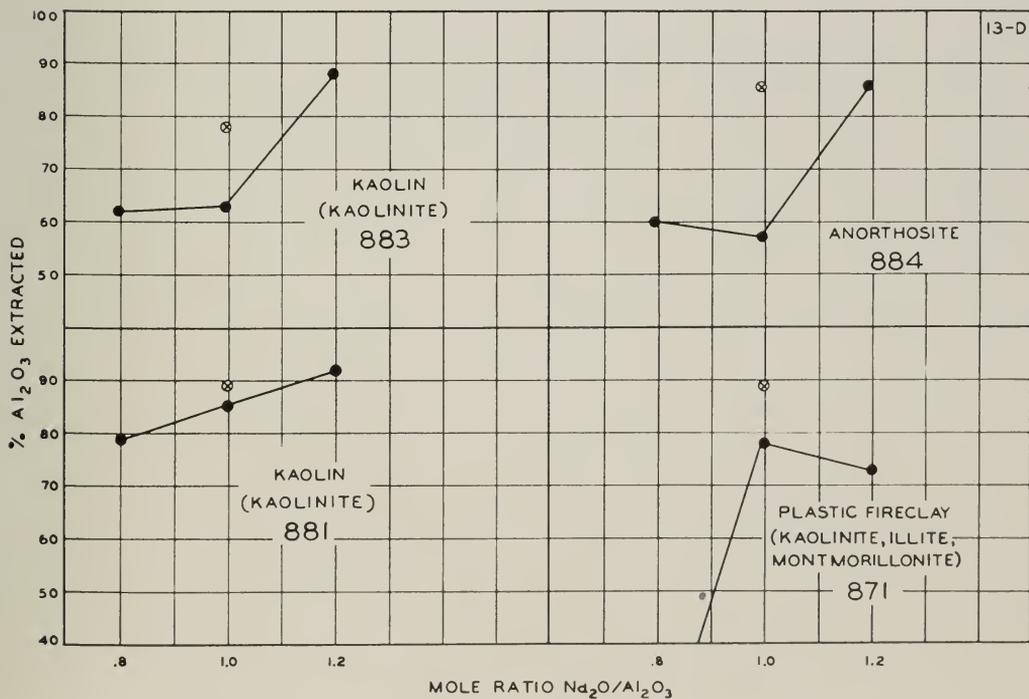
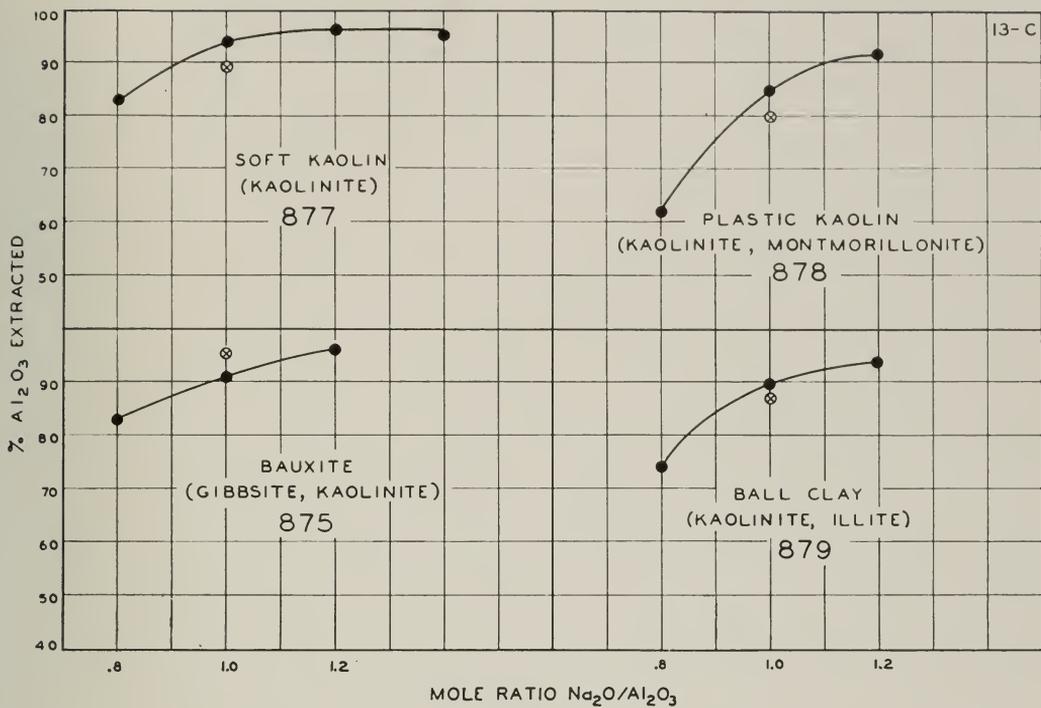


FIG. 13.—Parts C and D  
 Percent  $\text{Al}_2\text{O}_3$  extracted versus mole ratio  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$   
 Sinter temperature  $1200^\circ\text{C}$ .; sinter time 10 minutes at top temperature.

smaller particles than would a more friable material ground to pass the same sieve.

The typical kaolinite clays show somewhat less variation in alumina yield with increasing  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio than do impure kaolinite clays 871, 878, 879 or clays with imperfectly crystallized kaolinite, such as 869 and 883.

The illite clays reacted to variation in soda-to-alumina ratio in much the same way as did kaolinite and gibbsite-kaolinite clays.

The data for montmorillonite clay were erratic but it is probable that more extensive tests would give results similar to those obtained with illite clay.

Sinters prepared from the diaspora clay were rather insensitive to variation of  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio insofar as extraction yields were concerned.

Anorthosite showed considerable improvement in extractability with the high  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio.

#### EFFECT OF LIME-TO-ALUMINA RATIO

Data are presented graphically in figure 14 which indicate the variation of the percent alumina extracted with  $\text{CaO}/\text{SiO}_2$  ratios 1.8, 2.0, and 2.2. The  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio used was 1.0 in all cases except for kaolin 877 where it was 1.2. These sinters were burned at  $1200^\circ\text{C}$ . according to the schedule shown in figure 15.

Sinters prepared from kaolinite or illite clays give sharply reduced yields of alumina if the  $\text{CaO}/\text{SiO}_2$  ratio is less than two, but the yields are not improved by increasing the value of this ratio above two.

Sinters prepared from the montmorillonite clay showed improvement with excess lime. It is not clear why montmorillonite should react so differently as compared to other clays toward excess lime.

#### SILICA IN THE ALUMINA EXTRACT

Sinters from kaolinite clays gave alumina extracts in which the average values of the ratio  $100 \times \text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$  lie in the

range 2.0 to 2.3. The weight of the silica extracted from 10 grams of sinter averaged about 0.037 gram for pure kaolinite clays and somewhat less for imperfectly crystalline kaolins such as 869 and 883. Sintners from kaolinite clays which contained appreciable amounts of illite or montmorillonite showed less silica in their extract than did pure kaolins. High lime-clay ratios decreased the silica in the extracts from sintners prepared from kaolinite clays.

Sinters prepared from illite clays and montmorillonite clays gave extracts in which the average values of the ratio  $100 \times \text{SiO}_2/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$  were 2.3 to 3.2. The weights of silica extracted from ten grams of sinter averaged about 0.014 gram. High lime-clay ratios decreased the weight of silica in the extract in most cases.

Sinters prepared from halloyiste, diaspora, and gibbsite-kaolinite clays gave extracts in which the silica-to-alumina ratio was about the same as for kaolins.

Anorthosite was also much like kaolinite clays insofar as the amount of soluble silica in sintners prepared with it was concerned.

#### EFFECT OF MINOR COMPONENTS PRESENT IN THE RAW MATERIALS GENERAL COMMENTS

Practically all clays and limestones contain compounds of some or all of the elements iron, magnesium, titanium and phosphorous. Sinter mixes were prepared, burned, and extracted as described above with the exception that quantities of  $\text{Fe}_2\text{O}_3$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{TiO}_2$  and  $\text{MgCO}_3$  were added. The quantities were chosen so that the ranges likely to be encountered in naturally occurring clays or limestones would be covered. Clay 877 was chosen for the tests for the reason that it contained unusually small amounts of all of these substances except  $\text{TiO}_2$  and because it contained no clay mineral other than kaolinite. The tests were carried out at  $1150^\circ\text{C}$ . top temperature with a firing schedule as illustrated in figure 15. The data are presented graphically in figures 16, 17, 19, and 20.

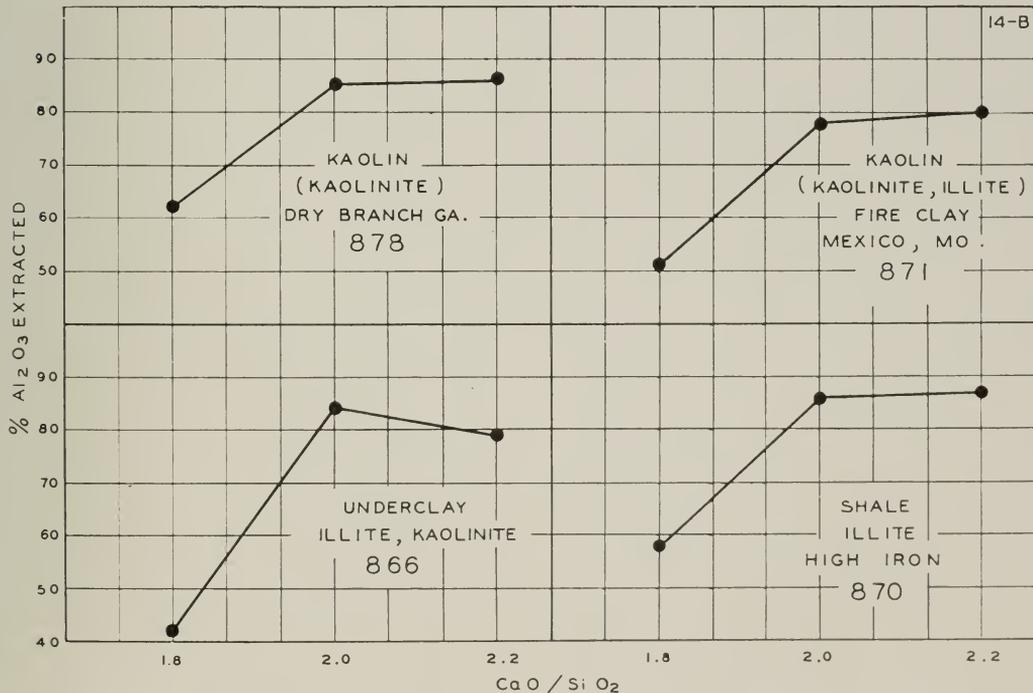
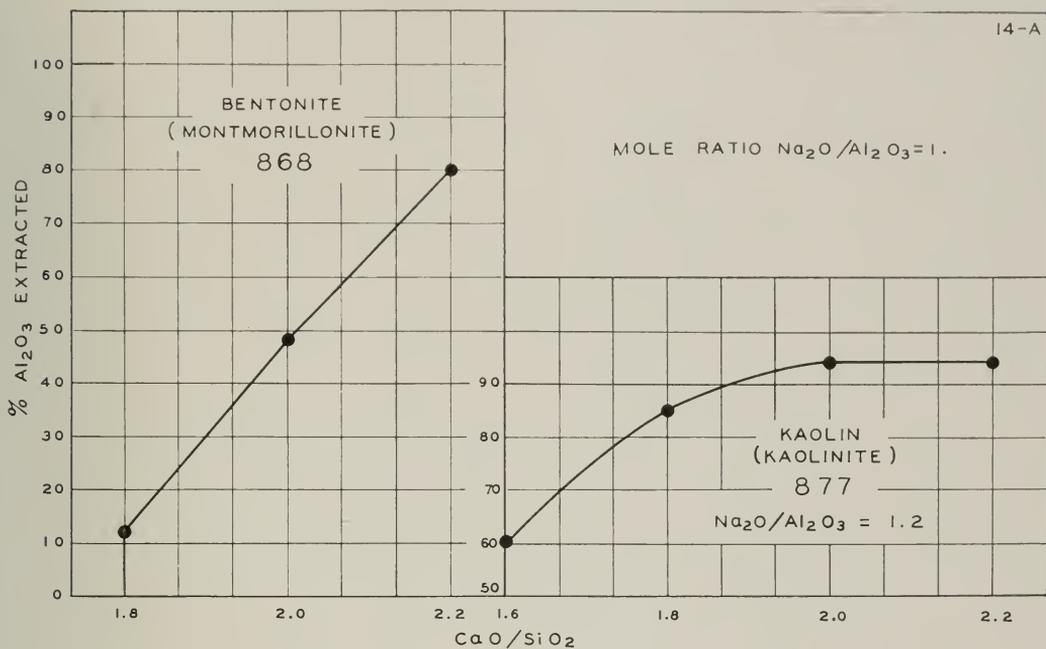


FIG. 14.—Parts A and B  
 Percent Al<sub>2</sub>O<sub>3</sub> extracted versus mole ratio CaO/SiO<sub>2</sub>  
 Sinter temperature 1200°C.; sinter time 10 minutes at top temperature.

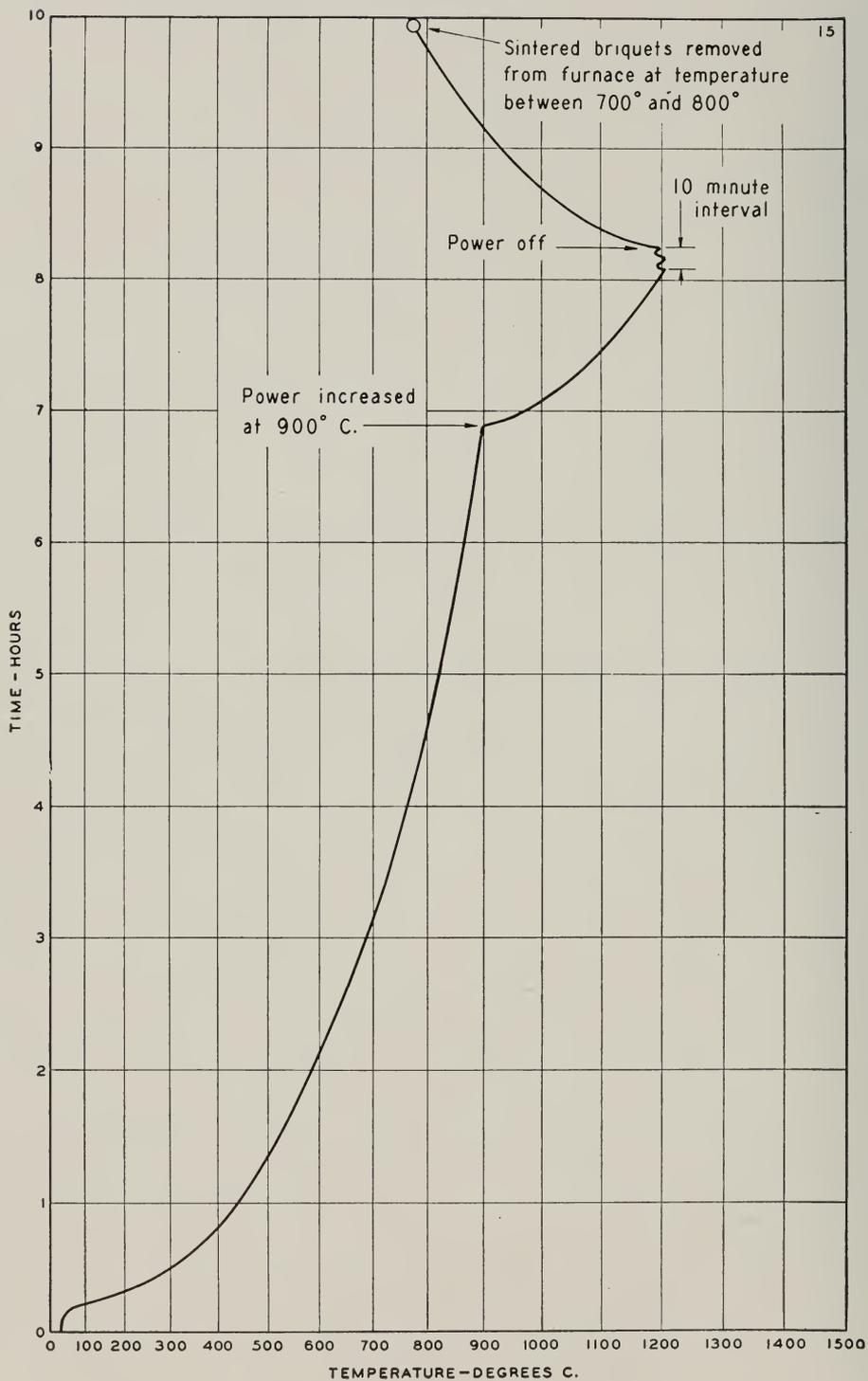


FIG. 15.—Typical record of a sinter heating schedule as traced from recorder chart.

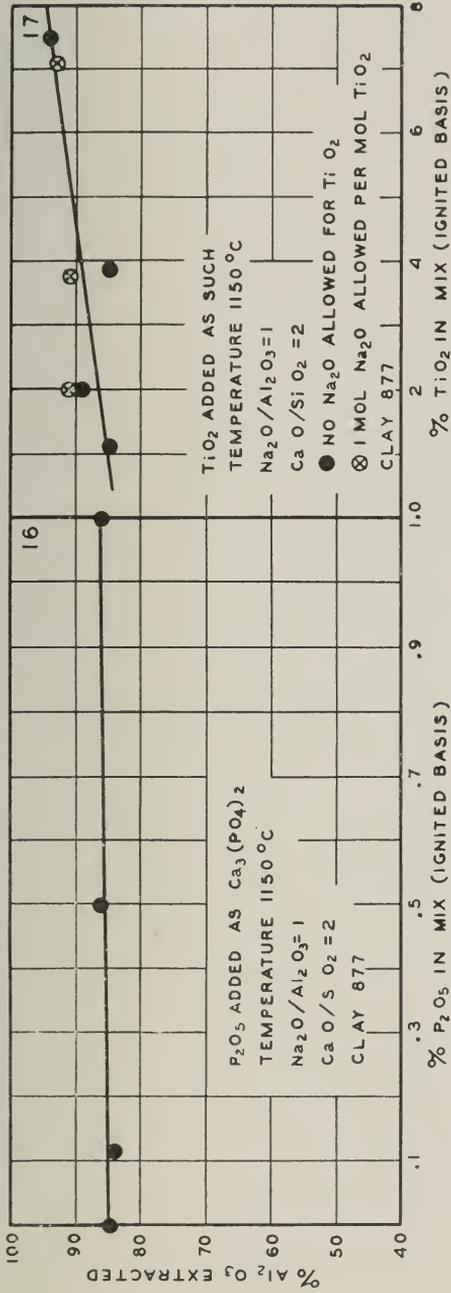


FIG. 17.—Percent  $\text{Al}_2\text{O}_3$  extracted versus  $\text{TiO}_2$  in mix.

FIG. 16.—Percent  $\text{Al}_2\text{O}_3$  extracted versus percent  $\text{P}_2\text{O}_5$  in mix.

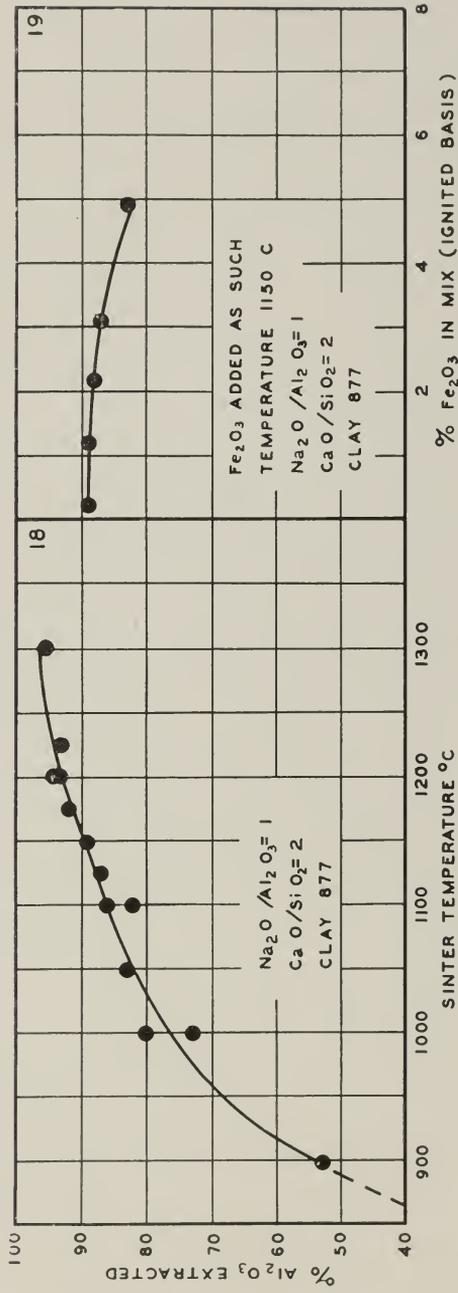


FIG. 18.—Percent  $\text{Al}_2\text{O}_3$  extracted versus sinter temperature.

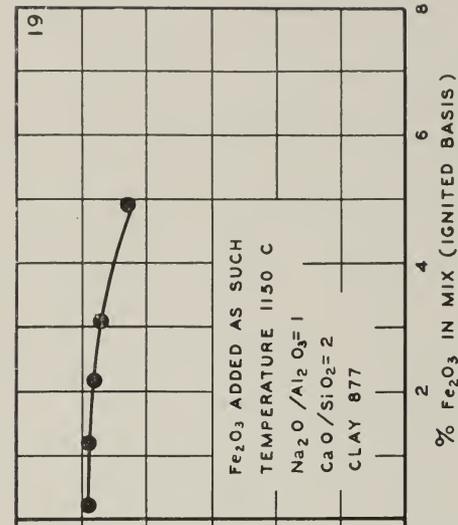


FIG. 19.—Percent  $\text{Al}_2\text{O}_3$  extracted versus percent  $\text{Fe}_2\text{O}_3$  in mix.

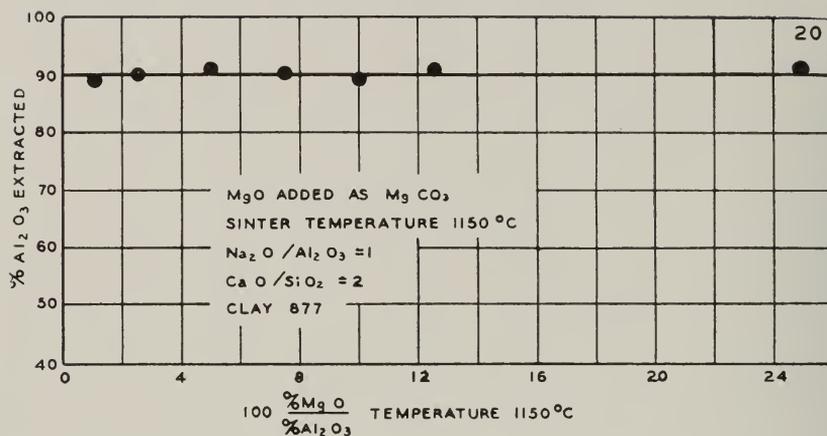


FIG. 20.—Percent  $\text{Al}_2\text{O}_3$  extracted versus  $100 \frac{\% \text{MgO}}{\% \text{Al}_2\text{O}_3}$  in sinter.

#### EFFECT OF PHOSPHORUS (Figure 16)

The data indicate that the presence of phosphate in quantities ranging up to one percent of the weight of sintered material exerts no important effect on the amount of  $\text{Al}_2\text{O}_3$  made extractable by lime-soda sintering. This is an expected result but is in contrast with results obtained when the lime only is used as the alkali in the sinter mix.

#### EFFECT OF TITANIA (Figure 17)

The results of these tests indicate that titania in the sinter is not harmful and may possibly have a small beneficial effect. There is a suggestion that it may be desirable to allow an extra mole of  $\text{Na}_2\text{CO}_3$  for each mole of  $\text{TiO}_2$  present. The variations in yield are, however, of the same order as the probable precision of the data.

#### EFFECT OF IRON (Figure 19)

Iron apparently has a moderate adverse effect on the yield of extractable  $\text{Al}_2\text{O}_3$ . This effect is not serious, however, unless three percent or more  $\text{Fe}_2\text{O}_3$  is present in the sinter.

#### EFFECT OF MAGNESIA (Figure 20)

The data indicate no effect of magnesia on the percent of extractable alumina even

when the amount of magnesia present is as much as 26 percent of the total alumina present in the sinter. This is markedly different from the results when the lime-sinter method is used.

## MINERALOGICAL ANALYSES

### MICROSCOPIC ANALYSIS

#### EFFECT OF VARIATIONS IN TOP SINTERING TEMPERATURE

Mixtures with a lime-to-silica ratio of 2.0 and a soda-to-alumina ratio of 1.0 were fired for 10 minutes under oxidizing conditions according to the schedule in figure 15.

*Kaolinite clay.*—New reaction products were very indistinctly developed in sinters fired to  $1000^\circ\text{C}$ ., and it appeared that the components had only started to react and that new phases had only begun to separate out (fig. 21C). Most of the material was an aggregate mass of faintly anisotropic material with an index of refraction about equal to 1.650. Some material, also slightly anisotropic, with an index of refraction of about 1.590 was present also.

Sinters fired at  $1200^\circ\text{C}$ . were composed of  $\beta\text{-C}_2\text{S}$  in grains with a maximum diameter of 3 microns, and a lesser amount of a slightly anisotropic material with a mean index of 1.590 that was interpreted as  $\text{C}_2\text{A}_3$  with considerable soda in solid solution.

The sinters fired to 1300°C. (fig. 21D) were similar to those fired to 1200°C. except that the  $\beta$ -C<sub>2</sub>S had a "cleaner" appearance. A possible interpretation is that  $\beta$ -C<sub>2</sub>S contains solid solution components at 1200°C. which separate out when the temperature is increased to 1300°C.

*Halloysite clay.*—Sinters prepared with this type of clay had the same characteristics as those made with kaolinite clay.

*Diaspore clay.*—Sinters fired at 1000°C. were composed largely of NA in irregular aggregate masses of individual units less than about 1 micron in diameter (fig. 21A). A small amount of  $\beta$ -C<sub>2</sub>S in grains with a maximum diameter of 3 microns was present also (the sample contained a little kaolinite and therefore some silica as an impurity).

Sinters fired to 1100°, 1200°, and 1300°C. had the same characteristics as the 1000°C. sinter (fig. 21B).

*Gibbsite-kaolinite (bauxite) clay.*—NA (Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>) was present in rather indistinct extremely minute grains, and some poorly developed  $\beta$ -C<sub>2</sub>S was found also in sinters fired to 1000°C.

Sinters fired to 1100°, 1200°, and 1300°C. all showed well developed NA in aggregates of units less than about 1 micron, and  $\beta$ -C<sub>2</sub>S in distinct grains with a maximum diameter of 5 microns.

*Illite clay.*—A mixture of particles of lime and dehydrated illite composed sinters fired at 1000° and 1100°C. (fig. 22A).

In sinters fired to 1200°C. the components were  $\beta$ -C<sub>2</sub>S in units with a maximum diameter of 15 microns, a pigmentary material with the characteristics of 4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub>, and a colorless faintly anisotropic interstitial material with a mean index of refraction of 1.60. The latter component was interpreted as C<sub>2</sub>A<sub>3</sub> with soda in solid solution (fig. 22B).

Sinters fired at 1300°C. were like those fired at 1200°C. except that the  $\beta$ -C<sub>2</sub>S had a "cleaner" appearance as if some solid solution components had separated out (fig. 22C).

*Montmorillonite clay.*—A mixture of particles of lime and dehydrated montmorillonite composed sinters fired at 1000° and 1100°C.

Sinters fired at 1200°C. were composed chiefly of  $\beta$ -C<sub>2</sub>S in units with a maximum diameter of 15 microns. A small amount of pigmentary material with the characteristics of 4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub> was present also. A component approaching C<sub>2</sub>A<sub>3</sub> may have been present, but it could not be positively identified.

C<sub>2</sub>S, chiefly  $\beta$ -form (there was some inversion to  $\gamma$ -form), in units with a maximum diameter of 15 microns made up about all of the 1300°C. sinter. The ferrite appeared to be less abundant, and the aluminate was less certain than in the 1200°C. sinter.

Attention should probably be directed to the fact that these and ensuing mineralogical comments relate only to crystallized observable phases. In many cases it is obvious that the lime content is insufficient to develop both a silicate and an aluminate for the entire silica and alumina contents with even the most generous allowances for soda solution.

#### EFFECT OF VARIATIONS IN THE RATIO OF SODA TO ALUMINA

The soda-to-alumina ratio was varied from 0.8 to 1.2, in sinters with a lime-to-silica ratio of 2.0 and fired to 1200°C. for 10 minutes under oxidizing conditions according to the schedule in figure 15.

*Kaolinite clay.*—Variations in the soda-to-alumina ratio from 0.8 to 1.2 caused no essential variations in the character of the sinters.

*Diaspore clay.*—Sinters prepared with a soda-to-alumina ratio of 1.2 were composed essentially of NA. They also contained a considerable amount of green-brown pigmentary material that has many of the characteristics of the ferrite, and it is suggested that the excess soda is held in some such compound. A small amount of  $\beta$ -C<sub>2</sub>S was present also.

An isotropic glassy material with an index of refraction roughly equal to the mean index of NA was the essential component in sinters prepared with a soda-to-alumina ratio of 0.8. A deficiency in soda appeared to hinder the crystallization of NA.

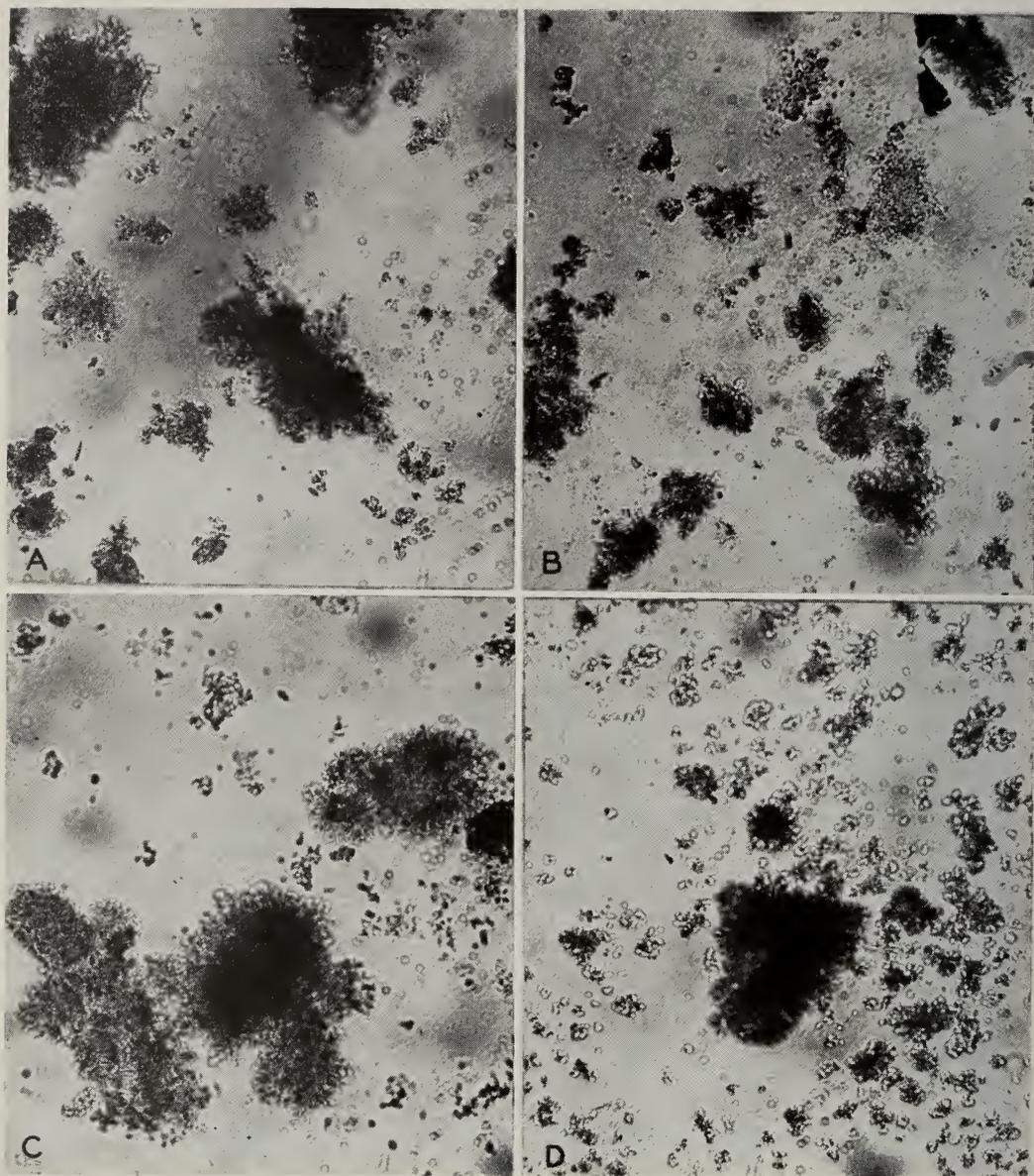


FIG. 21.—Photomicrographs of soda-lime-clay sinters, 300 $\times$ .

- A. Diaspore-clay sinter fired to 1000°C. showing aggregate masses of aluminates.
- B. Diaspore-clay sinter fired to 1200°C. showing aggregate masses of aluminates somewhat better developed than in A.
- C. Kaolinite-clay sinter fired to 1000°C. showing the development of some particles of new phases, and aggregate masses in which the formation of new phases is indistinct.
- D. Kaolinite-clay sinter fired to 1300°C. showing the distinct development of small particles of  $C_2S$  (mostly  $\beta$ -form). The aluminates are interstitial and indistinct.

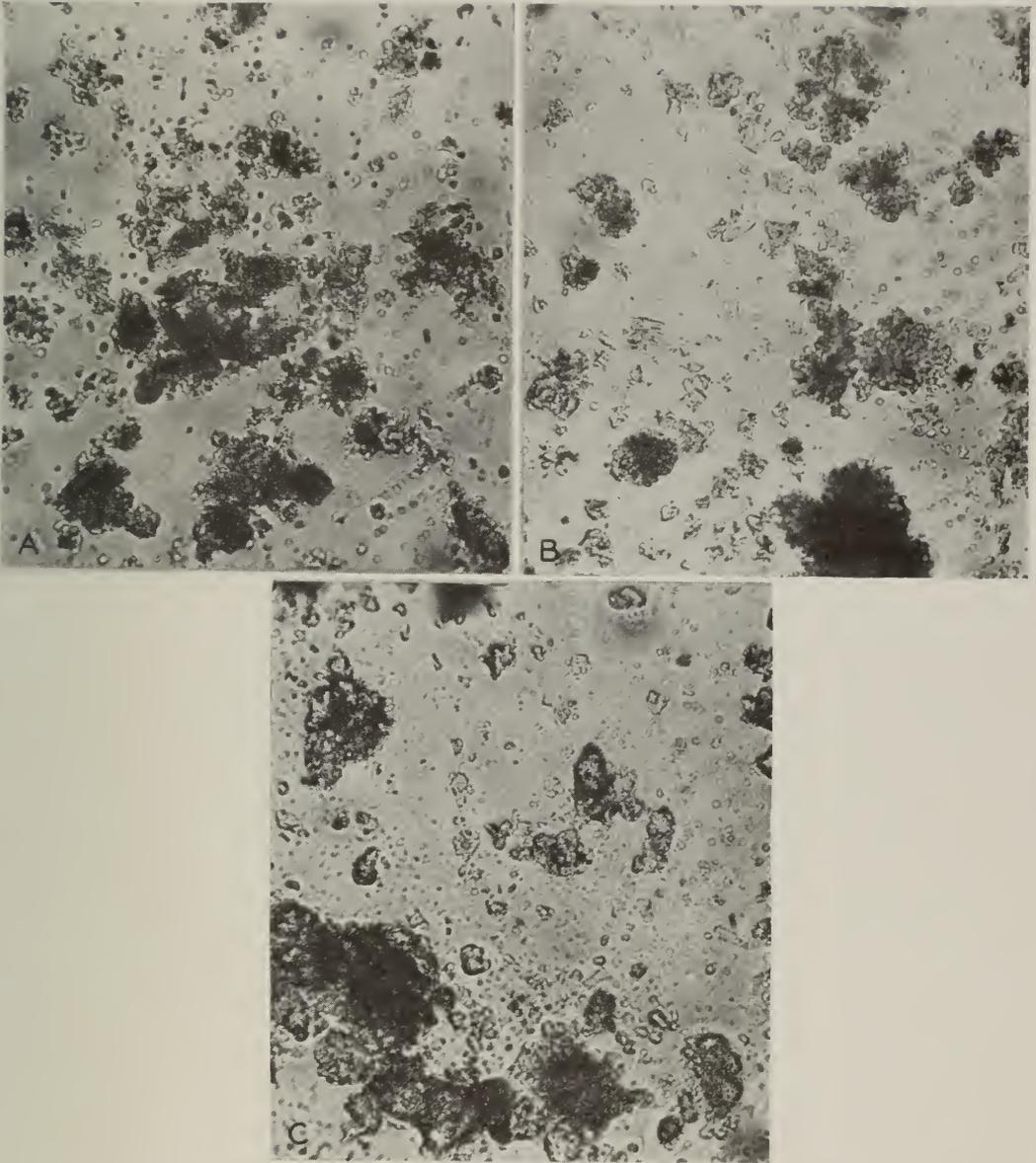


FIG. 22.—Photomicrographs of lime-soda-clay sinters, 300X.

- A. Illite-clay sinter fired to 1000°C. showing the absence of new phase development. Aggregate masses of dehydrated clay and lime are the components.
- B. Illite-clay sinter fired to 1200°C. showing the development of small particles of  $\beta\text{C}_2\text{S}$  and pigmentary ferrite. Large aggregate masses in which there is indistinct development of new phases are also present.
- C. Illite-clay sinter fired to 1300°C. showing the excellent development of large particles of  $\beta\text{C}_2\text{S}$  and pigmentary ferrite (dark material). An alumininate phase is not evident in the photomicrograph.

*Gibbsite-kaolinite (bauxite) clay.*—Sinters prepared with a soda-to-alumina ratio of 1.2 were composed of NA and  $\beta$ -C<sub>2</sub>S.

In sinters prepared with a soda-to-alumina ratio of 0.8, the component in addition to  $\beta$ -C<sub>2</sub>S was an isotropic glassy material with a mean index of refraction about equal to that of NA. Again the crystallization of NA appeared to be retarded by a deficiency of soda.

*Illite clay.*—An increase in the soda-to-alumina ratio from 1 to 1.2 caused the aluminate to be more prominent and to have properties more nearly approaching NA. Further, the C<sub>2</sub>S became "dirty" as if it had taken something into solid solution.

In sinters prepared with soda equivalent to 0.8,  $\beta$ -C<sub>2</sub>S, dirty in appearance, seemed to be about the only component. Aluminate could not be identified positively.

*Montmorillonite clay.*—Increasing the soda-to-alumina ratio from 1 to 1.2 caused a distinct increase in the prominence of the aluminate and gave it properties more nearly approaching NA. Further, the C<sub>2</sub>S in such sinters was "dirty" in appearance.

A decrease in the soda-to-alumina ratio from 1 to 0.8 was attended by a decrease in the abundance of aluminate and a trend toward material with the characteristics of C<sub>5</sub>A<sub>3</sub>. Further, the C<sub>2</sub>S was distinct and "clean" in units to 10 microns in diameter.

#### EFFECT OF MISCELLANEOUS VARIATIONS IN COMPOSITION

Varying amounts of Fe<sub>2</sub>O<sub>3</sub>, MgCO<sub>3</sub>, TiO<sub>2</sub>, and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> were added to batches prepared with kaolinite clay 877 with a lime-to-silica ratio of 2, and soda-to-alumina ratio equal to 1. The sinters were fired at 1150°C. for 10 minutes under oxidizing conditions.

The sinter with the added Fe<sub>2</sub>O<sub>3</sub> contained a considerable amount of minute discrete particles of iron oxide. There was no suggestion that the iron had reacted with any of the other components.

No distinct phase containing TiO<sub>2</sub> could be detected in the sinters to which this component was added. However, the C<sub>2</sub>S and aluminate phases were much less distinct,

suggesting that the TiO<sub>2</sub> had hindered their development.

The sinter with added magnesia up to 26 percent of total alumina, and phosphate up to 1 percent of total sintered material were like those without these added components.

#### EFFECT OF REDUCING ATMOSPHERE

Sinters with a soda-to-alumina ratio of 1 and a lime-to-silica ratio of 2 were fired to 1200°C. under reducing conditions according to the heating schedule given in figure 15.

*Kaolinite clays.*—Sinters fired under reducing conditions were essentially the same as those fired under oxidizing conditions except that under the former conditions the new phases were better developed. Further, when any iron compound was present in the clay as an impurity, the aluminate in the sinter fired under reducing conditions had a dirty yellowish appearance and a higher index of refraction indicating that iron was held in solid solution.

*Gibbsite and diaspore clay.*—If the clay contained any iron component as an impurity, the aluminate in sinters prepared under reducing conditions was dirty in appearance and had a higher index of refraction, indicating the presence of iron in solid solution.

*Illite clay.*—The sinters fired under reducing conditions exhibited an absence of any material that appeared unreacted and an enhanced development of new phases. The  $\beta$ -C<sub>2</sub>S developed in units with a maximum diameter of 20 microns as compared to 10 microns in sinters fired under oxidizing conditions. Further the aluminate was more distinct and had characteristics suggesting that iron had been taken into solid solution.

*Montmorillonite clay.*—Sinters prepared under reducing conditions showed a larger percentage of definitely reacted material and better development of new phases. The  $\beta$ -C<sub>2</sub>S was present in cleaner and larger units (20 microns  $\pm$ ), and the aluminate appeared to have taken iron into solid solution.

EFFECT OF VARIATION IN TIME BATCH HELD  
AT TOP SINTERING TEMPERATURE

Sinters prepared with a soda-to-alumina ratio of 1 and a lime-to-silica ratio of 2 were heated according to the regular firing schedule shown in figure 15 to 1100°C. One batch of sinters was held at 1100°C. for 10 minutes, another batch for 60 minutes, and a final batch for two hours.

*Kaolinite clay.*—Only a slight difference could be detected between the sinters fired for 10 minutes and those fired for two hours. The 10 minute sinter was composed of a small amount of material that seemed unreacted and material that appeared to be in the initial stage of reaction. The two hour sinters showed a more advanced degree of reaction with better development of new phases.

*Gibbsite and diaspore clays.*—Sinters fired at 10 minutes and at two hours both showed complete reaction of components with the development of new phases.

*Illite clay.*—The sinter held at 1100°C. for two hours was composed of unreacted components with a small amount of material that might have been in the initial stages of reaction. The 10 minute sinter was composed almost entirely of unreacted material.

*Montmorillonite clay.*—Sinters fired at 10 minutes and at two hours were both composed of essentially unreacted material.

## EFFECT OF VARIATION IN HEATING RATE

The following data were determined on sinters with a lime-to-silica ratio of 2 and a soda-to-lime ratio of 1 fired under oxidizing conditions, with a heating schedule of 50°C. per hour over the range from 900° to 1100°C. instead of the more rapid and standard rate shown in figure 15.

*Kaolinite clay.*—The  $C_2S$  and aluminate appeared to be more distinct and in better developed units in the sinters prepared at the slower heating rate. The aluminate showed more distinct anisotropism, and the  $C_2S$  was more definite and "cleaner", suggesting less solid solution effects. Also there seemed to be more inversion of  $C_2S$  to the  $\gamma$ -form.

*Gibbsite and diaspore clays.*—The sinters prepared at the slower heating rate were usually about the same as those prepared at the regular heating rate. In a few instances there was a suggestion of better phase development with the slower heating rate. Also, any  $C_2S$  present, because of the presence of a silicate mineral in the clay, showed more inversion to the  $\gamma$ -form.

*Illite and montmorillonite clays.*—No difference could be detected between sinters prepared at the regular and at the slow rate.

The more friable character of many of the sinters (see page 57) prepared with the slower heating rate was in accord with the slightly better phase development and the greater degree of inversion of  $C_2S$  to the  $\gamma$ -form.

EFFECT OF VARIATIONS IN THE RATIO OF  
LIME TO SILICA

The lime-to-silica ratio was varied from 1.8 to 2.2 in sinters with a soda-to-alumina ratio of 1, and fired to 1200°C. for 10 minutes under oxidizing conditions according to the heating schedule given in fig. 23.

*Kaolinite and illite clays.*—The sinters showed that the best phase development took place when the lime-to-silica ratio was 1.8. In such sinters the  $\beta$ - $C_2S$  was in distinct units, and the aluminate, which approaches  $C_3A_3$  in optical properties, was plainly visible.

As the lime content increased, there was a decrease in the degree of phase development. For example, sinters with a lime-to-silica ratio of 2.0 frequently contained a considerable amount of material in aggregate masses of indistinct units with about the optical properties of  $\beta$ - $C_2S$  but with few distinct grains of  $\beta$ - $C_2S$ . Also the aluminate was less distinct and closer to  $C_3A_3$  in optical properties.

With an increase in the lime-to-silica equal to 2.2 there was a further slight decrease in the degree of development of phases.

*Montmorillonite clay.*—In sinters prepared with clays containing montmorillonite, there appeared to be little or no dif-

ference in characteristics when the lime-to-silica ratio was varied from 1.8 to 2.2.

## X-RAY ANALYSIS

### GENERAL COMMENTS

In the application of the X-ray diffraction method to the lime-soda sinters, two unsatisfactory situations must be admitted: first, it is uncertain whether all of the phases in the four-component system are known, and second, the extent to which various solid solution possibilities may be realized cannot be established. Diffraction patterns are frequently not precisely typical for a given phase, and should therefore not be relied upon for estimates of abundance of the phase.

### THE PHASES

*Calcium orthosilicate.*—The lime-soda sinters do not dust. In none of the sinters examined did enough orthosilicate invert to the  $\gamma$ -form so that the  $\gamma$ - $C_2S$  could be found by diffraction methods. The development of  $\beta$ - $C_2S$  was essentially parallel to the development outlined in the lime-sinter discussion. In the lower temperature sinters (1000°C.) a considerable amount of reaction products was evident, the material being of extremely small particle size, and the diffraction pattern of that resulting phase which we consider to be the silicate departed from the typical  $\beta$ - $C_2S$  to such a degree that in ascribing the pattern to  $\beta$ - $C_2S$  we could be in error. For the kaolinite sinters, development of this phase was gradual, and by 1200°C. the pattern was typical for  $\beta$ - $C_2S$  whose particle size is about of the order of a micron. In the illite and montmorillonite clay sinters the same material developed abruptly above about 1200°C. and by 1300°C. attained a particle size of 25 to 50 microns.

The large  $\beta$ - $C_2S$  grains, which did not invert, no doubt held some extraneous ions in solution. The low temperature  $\beta$ - $C_2S$  could vary from ideal composition to a much greater degree.

*Sodium aluminate.*—The sodium aluminate,  $NaAlO_2$ , is a well-established phase

for which the powder diffraction diagram is readily recognized but the crystallization has not been worked out. The phase was clearly developed and typical only in the sinters prepared with the highest alumina clays. In other cases, where the phase was observed at all, some lines had anomalous weak intensities or were missing, and the apparent abundance was not commensurate with the alumina content. It is our unsupported opinion that the typical NA is a variation of the cristobalite structure, and that the non-typical material is a combination of this with  $\gamma$ - $Al_2O_3$ . In some cases the development of NA was promoted by increased addition of  $Na_2CO_3$ .

*The complex aluminate.*—A prominent feature in the diffraction diagrams, especially of the kaolinite sinters at 1000° and 1100°C., was a pattern rather closely resembling that of  $C_5A_3$ . At higher temperatures, after the full development of  $\beta$ - $C_2S$ , this material was no longer apparent. In the  $CaO-Al_2O_3-Na_2O$  system, according to Brownmiller and Bogue,<sup>8</sup>  $C_5A_3$  does not dissolve soda. However, the published  $C_5A_3$  structure is of an open type, described as based on garnet, and it seems quite possible that soda and silica together could enter this crystallization. This material is assumed to be the nearly isotropic phase observed optically with the index 1.590.

The prominence of the above described pattern declined in sinters fired at 1200°C. and was not apparent at 1300°C. although it was still observed microscopically. One is led to the conclusion that the phase softened to a glass.

### THE SINTERING PROCESS

In the lime-soda sinters, reaction is initiated at somewhat lower temperatures than in the lime sinters. The softening of the sodium-calcium double carbonate (apparently represented in the thermal curves by a flexion near the shoulder of the decarbonization peak) provides a liquid agent for attack on the clay. High alumina materials, even the highly resistant  $\alpha$ - $Al_2O_3$ , react readily with the lime and soda, kaolinite

reacts less readily, and illite and montmorillonite react relatively little.

It was not possible to identify the first reaction product in sinters made with high aluminous clays, but at 1100°C., NA had developed. On further heating, the NA grew in grain size and had a typical diffraction pattern. Only a little  $\beta$ -C<sub>2</sub>S developed, as would be expected from the low silica content of these clays.

Kaolinite clay sinters have reacted at 1000°C. to form an extremely fine-grained mixture of the complex aluminate, "C<sub>5</sub>A<sub>3</sub>," and non-typical  $\beta$ -C<sub>2</sub>S. Continued heating gradually developed more  $\beta$ -C<sub>2</sub>S, which by the time the temperature reaches 1200°C. gave a typical diffraction pattern, while the crystalline structure of the complex aluminate was destroyed. The transition from the complex aluminate to the noncrystalline material was considered to be reflected in the greater extractability of aluminum in the higher temperature (or longer heated) sinters. The development of NA was either doubtful or unimportant in the sinters of kaolinite clays. When small amounts were indicated they appeared as well or better developed in the low temperature sinters as in the high.

In illite and montmorillonite clay sinters the complex aluminate, "C<sub>5</sub>A<sub>3</sub>," was less prominent. The  $\beta$ -C<sub>2</sub>S development, as in the case of the lime sinters, showed a sudden marked growth to large particle size when temperatures of 1200° or 1300° C. were reached. This growth was probably not significant in itself from the standpoint of extraction, but apparently reflected the greater difficulty of attack on these more stable clays.

#### DIFFERENTIAL THERMAL ANALYSES

Differential thermal analyses of batches of various types of clay with a lime-to-silica ratio equal to 2 and a soda-to-alumina ratio equal to 1 are given in figure 23.

The differential thermal curves show the relative intensity and the temperature of the reactions that take place when sinter mixtures are heated up to 1300°C. at a

uniform rate of approximately 10°C. per minute. The downward deflections of the curve indicate endothermic reactions and the upward deflections indicate exothermic reactions. A vertical scale for determining the temperature difference indicated by the deflections of the curve is given in figure 9.

*Diaspore clay 872, sinter mixture SS89.*—The endothermic reaction between 500° C. and 600°C. corresponds to the loss of lattice water (OH) from the diaspore. The part of the curve between 700°C. and 875°C. shows an endothermic reaction due to the loss of CO<sub>2</sub> from the carbonates plus an exothermic reaction which indicates the formation of a new phase. The curve characteristics that result when loss of CO<sub>2</sub> is the only reaction taking place in this temperature interval can be seen in curves for SS85 and SS87.

The curve for sinter mixture SS89 shows that a reaction is taking place between the components of the diaspore clay and the carbonates, and that a new phase or phases develop at about 800°C. The formation of the new phase begins before the reaction corresponding to the loss of CO<sub>2</sub> is complete.

The portion of the curve above 900°C. cannot be interpreted in detail, but it probably signifies changes in the form of the initial phases and/or the separation out of material held in solid solution.

*Gibbsite-kaolinite (bauxite) clay 875, sinter mixture SS90.*—The initial endothermic peak is due to loss of adsorbed water and suggests that halloysite as well as kaolinite is present in this clay. The endothermic peaks at about 340°C. and 590°C. are the result of loss of lattice water (OH) from gibbsite and kaolinite (and halloysite), respectively.

The endothermic peak between about 790°C. and 840°C. is the result of loss of CO<sub>2</sub> from the carbonates. However, if loss of CO<sub>2</sub> was the only reaction in this temperature interval, the curve should be like those of SS85 and SS87 in the same temperature interval. It can be concluded, therefore, that an exothermic reaction due to the formation of a new phase or phases

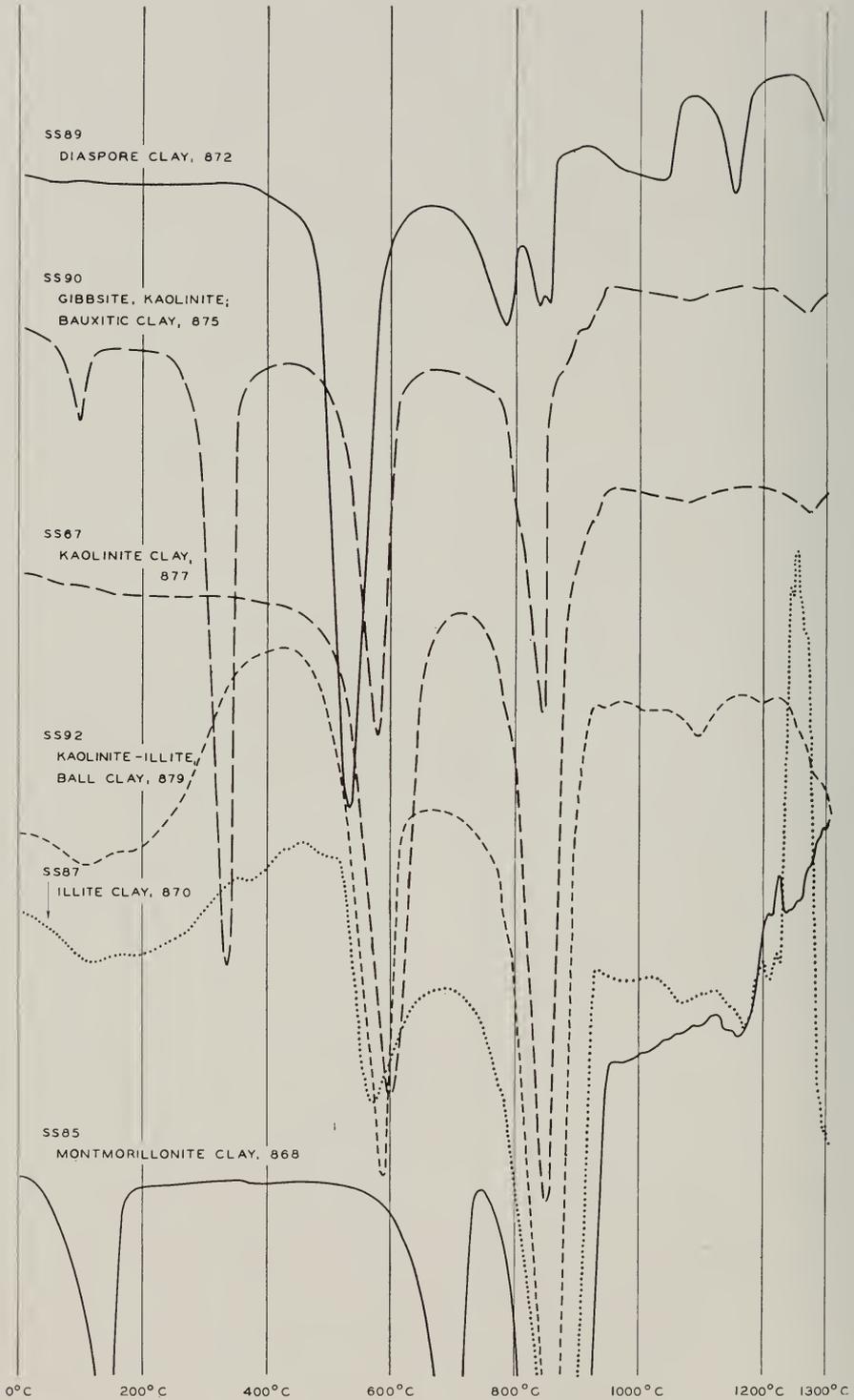


FIG. 23.—Differential thermal analyses of lime-soda-clay mixtures. The curves are composites from data for the clay alone and for sinter mixtures. (See fig. 9.)

begins soon after the start of loss of  $\text{CO}_2$ , i.e., about  $800^\circ\text{C}$ .

The curve above  $950^\circ\text{C}$ . is probably the result of changes in the initial phases and/or the separation out of material held in solid solution. It would seem that such changes take place without appreciable thermal effect. There appears to be no distinct thermal effect corresponding to the formation of the disilicate or the aluminate.

*Kaolinite clay 877, sinter mixture SS67.*—The endothermic reaction at about  $600^\circ\text{C}$ . corresponds to the loss of lattice water (OH) from the kaolinite. Again the endothermic reaction between about  $750^\circ\text{C}$ . and  $875^\circ\text{C}$ . is not as large as would be expected if loss of  $\text{CO}_2$  were the only reaction during this temperature interval. It is probable that  $\text{C}_2\text{S}$  and perhaps other phases begin to form before the destruction of the carbonate is complete. The new phases seem to develop at slightly higher temperatures in sinter mixes containing kaolinite clays than in those prepared with diaspore or gibbsite since the reaction due to loss of  $\text{CO}_2$  is less affected in such sinter mixes.

The curve above  $950^\circ\text{C}$ . is like that for batch SS90, and the same explanation is offered.

*Kaolinite-illite (ball) clay 879, sinter mixture SS92.*—In this curve the initial endothermic peak corresponds to the loss of adsorbed water by illite, the exothermic reaction between about  $200^\circ\text{C}$ . and  $500^\circ\text{C}$ . is the result of the burning off of organic material, and the endothermic peak at about  $600^\circ\text{C}$ . is caused by the loss of lattice water (OH) from the kaolinite and illite.

The portion of the curve between  $750^\circ$  and  $1000^\circ\text{C}$ . is about like that for the preceding sinter batch SS67 and the same reactions are indicated. The curve above  $1000^\circ\text{C}$ . has some slight differences which are like those in the curve for the batch containing illite (SS87), and show the influence of the small amount of illite in this clay.

*Illite clay 870, sinter mixture SS87.*—The broad initial endothermic reaction is due to loss of adsorbed water, and the endothermic peak at about  $575^\circ\text{C}$ . corresponds

to loss of lattice water (OH) from the illite.

The endothermic reaction between about  $700^\circ\text{C}$ . and  $925^\circ\text{C}$ . appears to be the result of a single reaction. Unlike the curves for the previous mixture, the removal of  $\text{CO}_2$  from the carbonate seems to be the only reaction taking place in this temperature interval.

The sharp exothermic reaction at about  $1200^\circ\text{C}$ . represents the formation of  $\text{C}_2\text{S}$  and perhaps other new phases. The temperature at which new phases form is several hundred degrees higher in sinter mixtures containing illite clays than in those made up of kaolinite, gibbsite, or diaspore clays. This is in accord with the extraction data which show very little alumina is extractable from illite clay sinters until firing temperatures reach  $1200^\circ\text{C}$ ., whereas a high percentage of alumina is extractable from sinters containing kaolinite, gibbsite, or diaspore when the firing has been carried to only  $1000^\circ\text{C}$ .

*Montmorillonite clay 868, sinter mixture SS85.*—The endothermic peaks at about  $150^\circ\text{C}$ . and  $700^\circ\text{C}$ . are due to loss of adsorbed water and lattice water (OH), respectively, from the montmorillonite. The portion of the curve above  $750^\circ\text{C}$ . is similar to that for the preceding mixture containing illite clay and the same reactions are indicated.

Like illite mixtures, batches containing montmorillonite do not yield new phases until a temperature of about  $1200^\circ\text{C}$ . is reached, and appreciable alumina is not extractable until sinters have been fired to this temperature.

#### DISCUSSION AND SUMMARY OF STUDY OF PHASES PRESENT IN THE SINTERS

The X-ray and optical data concurred in the conclusion that in sinters with a lime-to-silica ratio of 2 and a soda-to-alumina ratio of 1, the compound  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3$ , as described by Brownmiller and Bogue<sup>8</sup> is well developed only in sinters prepared with high alumina clays (containing diaspore or gibbsite). In kaolinite clays the aluminate appeared to be  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$  with soda and perhaps silica in solid solution. In illite and

montmorillonite clays the development of aluminate was very poor, but the compound again seemed to be more nearly like  $C_3A_3$ .

Soda in excess of that required for a ratio of soda to alumina equal to one caused an enhanced development of aluminate with characteristics more like NA. A decrease in the soda content caused a decrease in the development of aluminate and a trend toward characteristics like those of  $C_3A_3$ .

The  $C_2S$  occurred in distinct units only a few microns in diameter in sinters made with kaolinite clay. In sinters made with illite or montmorillonite clays, the  $C_2S$  attained a maximum diameter of over 20 microns. The  $C_2S$  was in the  $\beta$ -form with little inversion to the  $\gamma$ -form.

The aluminate was found in irregular aggregates and interstitial masses composed of indistinct individual units less than one micron in diameter.

In sinters prepared with gibbsite or diaspore clays new phases began to develop as soon as loss of  $CO_2$  released  $CaO$  and  $Na_2O$ , or perhaps sooner, under the attack of the fluid double carbonate, hence a large percentage of alumina was extractable in sinters made at low temperatures, e.g.,  $1000^\circ C$ . Again in sinters made with kaolinite clays, new phases began to form before the carbonates were completely broken down although it would seem that the temperature was slightly higher than for the gibbsite or diaspore clays. As a consequence sinters containing kaolinite clay and fired at low temperatures had high percentages of extractable alumina. In the kaolinite and gibbsite clays the phases appeared to continue to develop throughout a temperature interval of several hundred degrees, and without sharp thermal effects.

When sinters were prepared containing illite or montmorillonite clays, new phases did not develop extensively until about  $1200^\circ C$ . and consequently little alumina was extractable unless the firing was carried to this temperature. Further there was a sharp thermal reaction which began at about  $1175^\circ$  corresponding to the formation of the new phases in illite and montmorillonite clay mixtures.

A plausible explanation for the difference in temperatures required for new phase development is as follows: In the case of gibbsite and diaspore the loss of (OH) water at about  $325^\circ C$ ., and  $525^\circ C$ ., respectively, results in the formation of free alumina which appears to be particularly susceptible to attack by fluid double carbonates. As a consequence new phases form at a very low temperature. The loss of (OH) lattice water from kaolinite at about  $575^\circ C$ . produces the active, but still crudely combined alumina and silica of metakaolin, and new phases are formed slightly later, after considerable development of free lime.

In the case of montmorillonite and illite, the loss of (OH) water at  $575^\circ$  and  $675^\circ C$ ., respectively, is not accompanied by a destruction of the lattice of these minerals. A definite structural configuration is retained until a temperature is reached several hundred degrees in excess of that required for loss of (OH) water. It would be expected that alumina and silica locked up in a definite structural configuration would be relatively unreactable, and that new phases would not develop until such a configuration is destroyed. New phases, then, would not be expected in sinters prepared with illite or montmorillonite clays until a higher temperature is reached (or until after a more protracted heating interval) than is required for similar development in batches containing the other types of clay materials. It follows, of course, that in plant practice the presence of any illite or montmorillonite in a clay would raise the sintering temperature necessary for the best extraction.

All the data suggest that the new phases formed at low temperatures in the kaolinite, diaspore and gibbsite batches undergo changes as the temperature is raised. The  $\beta$ - $C_2S$  can be seen under the microscope to become "cleaner" in appearance in sinters fired to higher temperatures, as if the  $\beta$ - $C_2S$  were being freed of material in solid solution. The diffraction pattern of  $\beta$ - $C_2S$  is typical only in higher temperature sinters. In lower temperature sinters the pattern departs considerably from that typical for

this compound. The prominence of the pattern of the complex aluminate is reduced as the temperature of sintering is increased, suggesting that the material is reduced to a kind of glassy substance.

## SUMMARY AND CONCLUSIONS

The introduction of soda into the alkali extraction processes as practiced in the lime-soda method resulted in attack of the clay at temperatures much lower than when lime alone was used. When the clays were of the high alumina variety (diaspores and bauxites) fairly good extractions were obtained with sintering temperatures of 1000° C. Kaolinite-clay sinters required slightly higher temperatures, whereas sinters prepared from illite or montmorillonite clays had to be heated to temperatures in the range 1200° to 1300° C. to give satisfactory yields. Unless raw materials containing sufficient soda to carry the process are available there is little advantage in using the lime-soda as compared to the lime process with the two latter types insofar as sintering temperature is concerned.

Kaolinite clays and gibbsite-kaolinite (bauxitic) clays may yield above 90 percent of their alumina by the lime-soda process when they are relatively free from iron and other clay minerals. Halloysite clay, montmorillonite clay, and anorthosite may also yield over 90 percent of their alumina, but it is more difficult to get top yields. The highest yields for illite clays were 10 to 12 percent below those for the other clays. Yields for clays composed of mixtures of clay minerals were in agreement with results predicted from pure types.

Diaspore clays and gibbsite-kaolinite clays yielded nearly as much alumina on sintering to 1000° C. as to 1300° C. Pure kaolinite clays showed no increase in yield when sintered above 1100° C. other factors being the same, and yielded about 75 percent of their alumina when sintered to 1000° C. Montmorillonite clays yielded none of their

alumina on sintering to 1100° C., 50 percent on sintering to 1200° C., and 90 percent on sintering to 1300° C. Like montmorillonite clay, illite clay required sintering above 1200° C. for good alumina yields.

In sinters fired to 1100° C., increasing the time held at top temperature caused only slight increase in yield of alumina from diasporic clays, only moderate increases for clays composed of kaolinite, gibbsite, and halloysite, and very great improvement in the yield from illite clays. Regardless of sintering time, montmorillonite clays yielded no alumina on firing to 1100° C.

Sinters of the various clays fired under strong reducing conditions gave the same yield as similar sinters fired under oxidizing conditions.

Although some of the results are erratic, the data show definite improvement in the yield of alumina from all types of clay except the diasporic as the  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio increased from 0.8 to 1.2.

Sinters of kaolinite clay and illite clay gave sharply reduced yield when the  $\text{CaO}/\text{SiO}_2$  ratio was less than two, but not improved yields with a ratio above two. Montmorillonite clay showed greatly increased alumina yields with  $\text{CaO}/\text{SiO}_2$  ratio greater than two.

Extracts from illite clays and montmorillonite clay contained a slightly larger percent of silica than the extracts from other clays. Kaolinite clays which contained appreciable amounts of illite and montmorillonite gave extracts with lower silica contents than pure kaolinite clays, but the difference was small.

Addition of phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) or magnesia to a kaolinite clay batch does not affect the amount of extractable alumina. Added  $\text{TiO}_2$  also was not harmful, but the data suggest that an extra mole of  $\text{Na}_2\text{O}$  ought to be allowed for each mole of  $\text{TiO}_2$  present. Added  $\text{Fe}_2\text{O}_3$  had a moderate adverse effect that was serious when the amount was more than three percent.

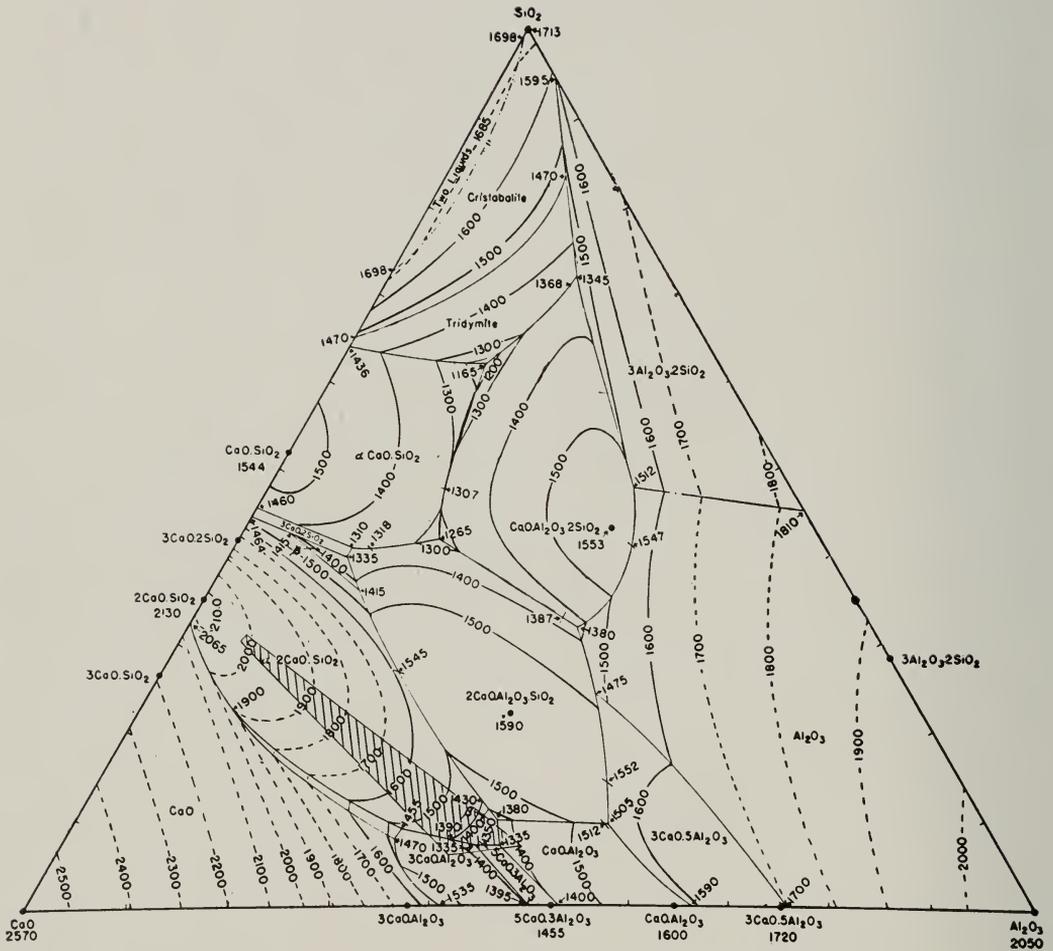


FIG. 24.—Equilibrium diagram of the system CaO—Al<sub>2</sub>O<sub>3</sub>—SiO<sub>2</sub>.

Diagram of Rankin and Wright revised by Schairer (see reference 9) and reproduced with his permission. Shaded area includes compositions of all lime sinter batches discussed in this report. Numbers represent temperatures in degrees C.

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